JOURNAL

OF

THE CHEMICAL SOCIETY.

Vol. LVIII. Part I.

1890. ABSTRACTS.

LONDON:
GURNEY & JACKSON, 1, PATERNOSTER ROW.
1890.

LONDON:
HARRISON AND SONS, PRINTERS IN ORDINARY TO HER MAJESTY,
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Vol. LVIII.

1890. ABSTRACTS.

LONDON:
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1890.

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Analytical Chemistry.

INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

1. Before beginning to write an abstract, it is desirable to read through the whole of the original paper, in order to form a judgment as to its importance, and as to the scale on which the abstract should accordingly be made.

2. The abstract should mainly consist of the expression, in the abstractor's own words, of the substance of the paper.

3. The abstract should be made as concise as possible, consistently with a clear and accurate statement of the author's results or theories, due regard being paid to their import.

4. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should as a rule be made of this fact. Important references to the researches of others quoted by an author should be reproduced in the abstract. Always employ figures instead of Roman numerals for references, thus:—*Annalen*, **221**, 92, instead of ccxxi, 92.

5. If an abstractor is acquainted with papers previously published by other authors containing statements either practically identical with, or opposed to, those in the paper abstracted, and to which no reference is made, he should notice their agreement or contradiction in a foot-note.

6. As a rule, details of methods of preparation or analysis, or generally speaking of work, may be omitted, unless such details are essential to the understanding of the results, or have some independent value.

Nomenclature.

7. Employ names such as *sodium chloride*, *potassium sulphate*, *ethyl acetate*, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chloride, sulphurous and sulphuric acid.

8. Term compounds of metallic and alcoholic radicles with the group OH, *hydroxides* and not hydrates; for example, potassium hydroxide, phenyl hydroxide, the name hydrate being reserved for compounds supposed to contain water of combination or crystallization. Compounds such as CH_3ONa, C_2H_5ONa, $C_7H_{15}ONa$, &c., should be termed sodium methoxide, ethoxide, heptyloxide, &c.

9. Apply the term *acid* only to compounds of hydrogen with negative radicles, such as HNO_3, H_2SO_4, H_3PO_4, and denote the oxides which form acids by names such as sulphuric anhydride, carbonic anhydride. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as hydrogen sodium sulphate, hydrogen disodium phosphate, &c., to the acid salts. Basic salts are as a rule best designated merely by their *formulæ.*

10. Use names such as *methane*, *ethane*, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3{\cdot}[CH_2]_5{\cdot}CH_3$, &c. The isomeric hydrocarbons are usually most conveniently represented by names indicating their relation to methane; for example, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$ = propylmethane; $CH_3{\cdot}CH(CH_3)_2$ = isopropylmethaue or trimethylmethane; or, although less frequently, by names such as diisopropyl.

11. Term the hydrocarbons C_2H_4 and C_2H_2 *ethylene* and *acetylene* respectively (not ethene and ethine). Distinguish the homologues of ethylene, whenever possible, by names indicating their relation to it, such as methylethylene, dimethylethyleue, &c., denoting the di-derivatives of the form $C_nH_{2n+1}{\cdot}CH{:}CH{\cdot}C_nH_{2n+2}$ as α-, and those of the form $CH_2{:}C(C_nH_{2n+1})_2$ as β-compounds, thus: $CH_3{\cdot}CH{:}CH{\cdot}CH_3$ = α-dimethylethylene; $CH_2{:}C(CH_3)_2$ = β-dimethylethylene. Similarly, use names such as methylacetylene and dimethylacetylene for the homologues of acetylene of the form $CH{:}C{\cdot}C_nH_{2n+1}$ and $C_nH_{2n+1}{\cdot}C{:}C{\cdot}C_nH_{2n+1}$. Adopt the same *allene* for the hydrocarbon $CH_2{:}C{:}CH_2$, and indicate the relation which its homologues bear to it in the same manner as pointed out for acetylene.

12. Distinguish all alcohols, that is, hydroxyl-derivatives of hydrocarbons, by names ending in *ol*; such as quinol, catechol, resorcinol, saligenol, glycerol, erythrol, mannitol, instead of hydroquinone, pyrocatechin, resorcin, saligenin, glycerin, erythrite, mannite. Compounds which are not alcohols, but which are at present distinguished by names ending in *ol*, may be represented by names ending in *ole*, if a systematic name cannot be given. For example, write indole instead of indol: furfuraldehyde instead of furfurol; fucusaldehyde instead of fucusol. Ethers derived from phenols, such as $C_6H_5{\cdot}OCH_3$, &c., hitherto called anisol, anethol, &c., may be distinguished by names ending in *oïl*, as anisoïl and anethoïl.

Alcohols should be spoken of as mono-, di-, tri-, or n-*hydric*, according to the number of OH groups.

13. Compounds analogous to the acids of the lactic series containing the group OH should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups C_2H_5O, C_6H_5O, $CH_3{\cdot}COO$, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus

ethoxypropionic acid instead of ethyl-lactic acid; 3 : 4 diethoxybenzoic acid instead of diethylprotocatechuic acid; and acetoxypropionic acid instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen-atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, viz., $C_6H(C_2H_5)_2(OH)_2{\cdot}COOH$, and not $C_6H_3(OC_2H_5)_2{\cdot}COOH$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2{\cdot}COOH$.

14. The term *ether* should be restricted to the oxides of hydrocarbon radicles, and the so-called compound ethers should be represented by names similar to those given to the analogously constituted metallic salts (comp. 12).

15. Compounds of the radicle SO_3H should, whenever possible, be termed *sulphonic* acids, or failing this, *sulpho-compounds* : as benzenesulphonic acid, sulphobenzoic acid, and not sulfi-compounds. Compounds of the radicle $SO_2{\cdot}NH_2$ should be termed sulphonamides.

16. Basic substances should invariably be indicated by names ending in *ine*, as aniline, instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteids, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide, or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

Notation.

17. Equations should *be omitted* unless essential to the understanding of the results; they, as a rule, should *not* be written on a separate line, but should "run on" with the text.

18. To economise space, it is desirable: 1, that *dots* should be used *instead of dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula; 2, that formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^α for $CH_2{\cdot}CH_2{\cdot}CH_3$, Pr^β for $CH(CH_3)_2$, Ph for C_6H_5, Ac for $CO{\cdot}CH_3$, and Bz for $CO{\cdot}C_6H_5$; and 3, that formulæ should be written *in one line* whenever this can be done without obscuring their meaning. For example:

$$CCl_3{\cdot}CH(OEt)_2 \text{ instead of } CCl_3{-}CH{<}{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}}$$

$$[CCl_3{\cdot}CH(OH)]_2S \text{ instead of } {\begin{matrix}CCl_3{-}CHOH\\CCl_3{-}CHOH\end{matrix}}{>}S$$

$$CH_2 : CH_2 \text{ instead of } CH_2{=}CH_2$$

$$CH \vdots CH \text{ instead of } CH{\equiv}CH$$

$$CH \vdots C{\cdot}CH_2{\cdot}CH_2{\cdot}C \vdots CH \text{ instead of } \begin{array}{l}CH_2{-}C{\equiv}CH\\ |\\ CH_2{-}C{\equiv}CH\end{array}$$

$$CHMe : CHPr^\alpha \text{ instead of } CH_3{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$$

$COOH{\cdot}CH : CMe{\cdot}COOH$ instead of $\begin{array}{l} CH_3\text{—}C\text{=}CH \\ \quad\;\, | \qquad | \\ COOH \;\; COOH \end{array}$

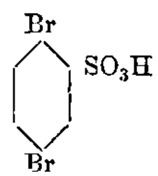
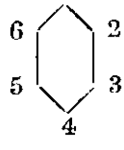
$CH_2Br{\cdot}CBrMe$ instead of $\begin{array}{c} CH_3CH_3 \\ \diagdown\diagup \\ CBr \\ | \\ CH_2Br \end{array}$

$CEt_2Ac{\cdot}COOEt$ instead of $\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ C{<}^{C_2H_5}_{C_2H_5} \\ | \\ COOC_2H_5 \end{array}$

$\begin{array}{l} CH_2{\cdot}CHMe \\ | \\ CH_2{\cdot}CHMe \end{array}{>}O$ instead of $\begin{array}{l} CH_2\text{—}CH{\cdot}CH_3 \\ | \qquad\quad \diagdown \\ | \qquad\quad\; {>}O, \\ | \qquad\quad \diagup \\ CH_2\text{—}CH{\cdot}CH_3 \end{array}$

$CHPh(OBz){\cdot}CH(OBz){\cdot}COOEt$ instead of
$C_6H_5{\cdot}CH(O{\cdot}CO{\cdot}C_6H_5){\cdot}CH(O{\cdot}COC_6H_5){\cdot}COOC_2H_5$.

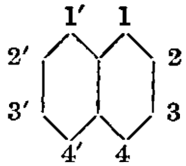
19. In representing the constitution of benzene-derivatives, as a rule, merely indicate the relative positions of the radicles in the symbol of benzene by figures, instead of by means of the hexagon symbol, for example:—

Paradibromobenzenesulphonic acid, $C_6H_3Br_2{\cdot}SO_3H$[Br : SO_3H : Br = 1 : 2 : 4] instead of  the figures always being used in the order 

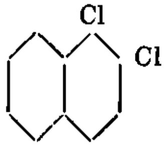
Relatively to the position 1, the positions 2 and 6 should always be spoken of as *ortho*-positions, 3 and 5 as *meta*-positions, and 4 as the *para*-position. It is better, however, in speaking of the derivatives of benzene, to express their constitution by giving them names such as 1 : 2 dibromobenzene, 1 : 3 dibromobenzene, &c., rather than by terming them ortho- or meta-dibromobenzene, &c.

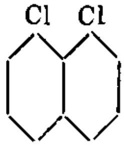
20. Moreover, in representing the constitution of derivatives of other "closed-chain" hydrocarbons do not, as a rule, employ graphic formulæ, but merely indicate the position of the radicles introduced in the following manner:—

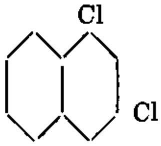
In the case of naphthalene, express the position of the radicles introduced in place of hydrogen relatively to the carbon-atoms common to the two "rings," and number the positions in the one ring 1, 2, 3, 4, and those in the other 1′, 2′, 3′, 4′ in the order shown by the annexed symbol:—

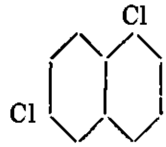


The dichloronaphthalenes, for example, are spoken of simply as 1 : 2 dichloronaphthalene, or dichloronaphthalene[Cl : Cl = 1 : 2], &c., thus:—

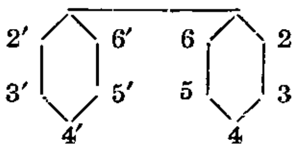
1 : 2 dichloronaphthalene = 

1 : 1′ dichloronaphthalene = 

1 : 3 dichloronaphthalene = 

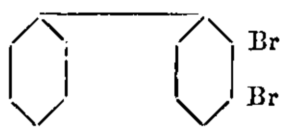
1 : 3′ dichloronaphthalene = 

In the case of diphenyl, indicate the position of the radicles relatively to the carbon-atom of one C_6 group which is associated with the other C_6 group, and number the positions in the one group by the figures, 2, 3, 4, 5, 6, and the corresponding positions in the other group by the figures 2′, 3′, 4′, 5′, 6′. as shown by the following symbol:

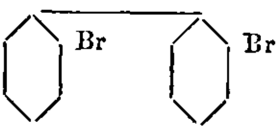


Thus the mono-derivatives, the bromodiphenyls, for example, are represented as

Bromodiphenyl [Br = 2]
" [Br = 3]
" [Br = 4]

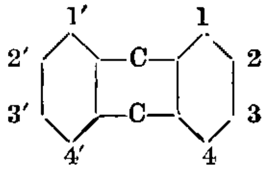
and the two dibromodiphenyls 

and



are respectively dibromodiphenyl [Br : Br = 2 : 3] and dibromodiphenyl [Br : Br = 2 : 6′].

In the case of anthracene, employ the following symbol, and indicate the position of the radicles relatively to the central C_2-group:



Examples:

Alizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 2].
Quinizarin, $C_6H_4 : C_2O_2 : C_6H_2(OH)_2$ [OH : OH = 1 : 4].
Anthraflavic acid, $C_6H_3(OH) : C_2O_2 : C_6H_3(OH)$ [OH : OH = 2 : 3′].

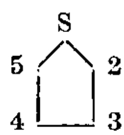
Purpurin, $C_6H_4 : C_2O_2 \cdot C_6H(OH)_3$ [OH : OH : OH = 1 : 2 : 4].

In speaking of compounds such as these, their constitution may be represented by the names

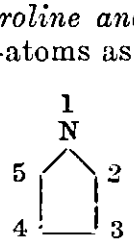
1 : 2 Dihydroxyanthraquinone = Alizarin.
1 : 4 ,, = Quinizarin.
2 : 3′ ,, = Anthraflavic acid.
1 : 2 : 4 Trihydroxyanthraquinone = Purpurin.

Always include the letters and figures indicating the constitution of derivatives of closed-chain hydrocarbons in square brackets.

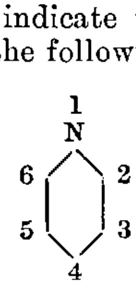
21. *In the case of thiophen*, express the position of the radicles introduced relatively to the sulphur-atom by numbers, as shown by the following symbol:



In the cases of pyrroline and pyridine, indicate the position relatively to the nitrogen-atoms as shown by the following symbols:

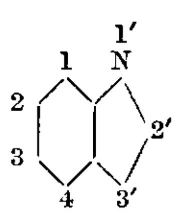


Pyrroline.

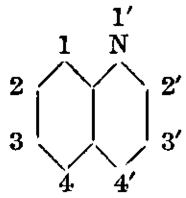


Pyridine.

In the case of indole, positions should be numbered as shown in the following symbol:—



In the case of quinoline, express the positions relatively to the carbon-atoms common to the two rings, and number the positions in the carbon ring 1, 2, 3, 4, and those in the nitrogen ring 1′, 2′, 3′, 4′ in the order shown by the annexed symbol :—



The Editor's decision, in all matters connected with the Abstracts, must be considered final.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Molecular Refraction. By H. LANDOLT (*Zeit. physikal. Chem.*, **4**, 413).—The author points out that Conrady's statements as to his method of determining the molecular refraction of the CH_2 group (*ibid.*, **3**, 212) are erroneous (compare Abstr., 1889, 661). H. C.

Heat of Neutralisation of Fluorides. By E. PETERSEN (*Zeit. physikal. Chem.*, **4**, 384—412).—The heats of neutralisation of the bases of the magnesium group, the alkali metals, and metals of the alkaline earths by hydrofluoric acid in solution are all equal, and for each molecule of hydrofluoric acid about 16300 cal. The above were determined by the interaction of the chlorides of the different metals with silver fluoride, and from the results the following heats of precipitation were also obtained: CaF_2, 2700 cal.; SrF_2, 2100 cal.; BaF_2, 1900 cal.; MgF_2 −2780 cal.; and AgCl 15900 cal.

The heats of neutralisation of the sesquifluorides of iron, chromium, vanadium, and manganese are—

$Fe_2(OH)_6,6HFAq.$	3×15830 cal.	$V_2(OH)_6,6HFAq.$	3×17410 cal.
$Cr_2(OH)_6$, ,,	3×16780 ,,	$Mn_2(OH)_6$, ,,	3×17210 ,,

With varying amounts of hydrofluoric acid up to 6 mols., the heat of neutralisation for the hydroxide of iron is proportional to the amount of the acid; for chromium and vanadium, it decreases slightly as the amount of acid increases. A further increase in the amount of acid produces a slight development of heat in the case of iron, vanadium, and chromium, but no effect whatever with manganese fluoride. The avidity of hydrofluoric acid towards ferric hydrate is three times as great as that of hydrochloric acid. H. C.

Exact Determination of the Melting Point of Organic Substances. By H. LANDOLT (*Zeit. physikal. Chem.*, **4**, 349—371).—

The author has made a comparison of the following methods for determining the melting point of organic substances:—

1. Melting and solidifying of large quantities of substance in which the thermometer is directly placed.
2. Heating the substance in a capillary tube.
3. Heating a platinum wire which has been covered with the substance in a mercury bath until, on melting, contact between the two metals is established, and an electric circuit thus closed.

The actual determinations made by the three methods were as follows:—

Method.	Naphthalene.	Mannitol.	Anthracene.
1. (Melting point)	80·04°, 80·10°	165·73°	200·61°
(Solidifying point)....	79·99°, 80·03°, 80·03°, 80·06°	165·64°, 165·69°	—
2. (Wide tube)	79·83°, 79·84°, 80·10°	167·54°	202·38°
(Narrow tube)	80·49°, 80·50°, 80·62°	—	—
3.	80·01°, 80·37°, 80·39°	165·77°, 166·92°	205·22°–207·62°
....	80·92°, 82·05°	167·04°	—

From the above results, more particularly those with naphthalene, the author concludes that the first method is the only one which will in all cases lead to accurate results. If this method is used, the solidifying point is most easily observed. The capillary tube method generally gives results that are too high, more especially when narrow tubes are used, and the electrical method is open to the same objection.

H. C.

Physical Constants of Halogen Substitution-products of Benzene and Toluene. By K. Seubert (*Ber.*, **22**, 2519—2524).—The author has determined the specific gravity of various halogen substitution-products of benzene and toluene, and the results are given in the following table as compared with water at 0°, 4°, and 20°, and in the last column as reduced by Winkelmann's formula for a temperature of 4° and a vacuum.

	t°.	0°.	4°.	20°.	4°. Reduced to a vacuum.
Chlorobenzene	20°	1·10726	1·10701	1·10855	1·10644
Bromobenzene	20°	1·49124	1·49095	1·49297	1·48972
Iodobenzene	20°	1·83247	1·83206	1·83460	1·82937
Orthochlorotoluene	20°	1·08198	1·08173	1·08323	1·08120
Metachlorotoluene........	20°	1·07242	1·07218	1·07367	1·07166
Parachlorotoluene	20°	1·06998	1·06974	1·07123	1·06923
Orthobromotoluene	20°	1·42252	1·42220	1·42417	1·42112
Metabromotoluene	20°	1·41019	1·40988	1·41183	1·40882
Parabromotoluene........	32°	1·39008	1·38977	1·39169	1·38832

The specific and molecular refractive power of these compounds was

also determined with an Abbe's refractometer. The values obtained are given in a table, and agree very closely on the whole with those calculated from the values for the atomic refractive powers given by Conrady (Abstr., 1889, 661), but they are in all cases a little too low. The experimental results were in accordance with Brühl's value of the refractive power of the double linking, and also showed that place-isomerism has very little or no influence on the molecular refractive power. The ortho-compounds seem to have the smallest molecular refractive power, that of the meta- and para-series being somewhat larger, and probably the same for both.

Parachlorotoluene melts at 7·4°, parabromotoluene at 26·2°. Chloro-, bromo-, and iodo-benzene, orthochloro-, orthobromo-, and metabromotoluene solidify when cooled with solid carbonic anhydride; metachlorotoluene does not solidify until cooled with solid carbonic anhydride and ether, but it remains solid in carbonic anhydride alone.

F. S. K.

Reciprocal Influence on the Solubility of Salts. By W. Nernst (*Zeit. physikal. Chem.*, **4**, 372—383).—The author regards the process of dissolution as being perfectly similar to that of vaporisation, the molecules assuming in both cases the gaseous state, in the one under the action of the osmotic pressure, in the other under that of the vapour-tension. On the Van't Hoff hypothesis it may, in fact, be shown that the work necessary to convert the gram-molecule of a salt into gas is equal to that required to bring the same amount of salt into solution. This work is the same for all substances, and hence it appears that the specific attraction between salt and solvent which has hitherto been assumed, does not exist, but that the process of dissolution is independent of such influences and similar in all cases.

The distribution of any vapour takes place in the atmosphere of an indifferent gas as in a vacuum, and in the same manner the solubility of a salt is not affected by the presence of a second salt in the solvent provided the two are without chemical action the one on the other. In the case of a dissociated vapour, however, Horstmann has shown that the addition of either of the products of dissociation will bring about an increase in the dissociation tension of that product, which causes a recombination and separation of a portion of the original substance, an effect which an indifferent gas is incapable of producing. In the same way the addition of either of the ions to an electrolyte in solution should bring about an increase in the osmotic pressure of that ion, and cause a separation of a portion of the salt from the solution, since an electrolyte in solution may be compared to a dissociated vapour. That this is the case is readily proved, for the addition of a concentrated solution of potassium chloride or hydroxide or of sodium chlorate to one of potassium chlorate immediately causes a separation of some of the latter salt, this being due in the one case to the presence of an excess of the positive, in the other to an excess of the negative ions. The amount of solid salt thus separated by the addition of a definite quantity of a second salt containing one of its ions, can be calculated from the dissociation theory, and the author shows the agreement between the calculated and observed quantities in the case of silver acetate.

H. C.

Sudden Changes in the Solubility of Salts caused by the Formation of two Layers in the Liquid. By H. W. B. Roozeboom (*Rec. Trav. Chim.*, **8**, 257—272).—In studying the conditions of equilibrium between a dissolved salt and water, a disturbing influence may be introduced, owing to the separation of the liquid into two layers of different concentrations. Cases of this sort are of frequent occurrence with organic compounds, and have been noticed by Alexéeff (Abstr., 1886, 847). The formation of two layers in a liquid is a change that is conditioned by temperature, and at certain temperatures it might be possible for the solid salt and the two liquid layers to exist side by side in equilibrium with one another and with the vapour of the liquid. Such temperatures, at which the simultaneous existence of the four phases is possible, would be indicated on the pressure curves as quadruple points (Abstr., 1888, 1511). The author has endeavoured to obtain experimental evidence in this direction, but could find no salt suitable for the purpose. H. C.

Determination of Affinity Coefficients. By W. Hecht, M. Conrad, and C. Brückner (*Zeit. physikal. Chem.*, **4**, 272—318).—Continuing their determination of affinity coefficients (Abstr. 1889, 931), the authors have examined the actions of sodium methoxide, ethoxide, and propoxide on the iodides of methyl, ethyl, propyl, and heptyl. The coefficients for methyl iodide are found to be in each case much greater than those of the other alkyl iodides, although the latter are also found to decrease somewhat with rising molecular weight. The relation between the coefficients of the iodides depends at the same time on the nature of the metallic salt, as may be seen by the following tables of these relations, in each of which the coefficient of heptyl iodide has been taken as unity.

	$C_2H_5 \cdot ONa$.	$C_3H_7 \cdot ONa$.	$CH_3 \cdot ONa$.
$C_7H_{15}I$	1·0	1·0	1·0
C_3H_7I	1·63	1·52	1·33
C_2H_5I	4·65	4·97	3·32
CH_3I	58·80	71·14	21·63

On the other hand, the influence of the metallic salt is greatest for the ethoxide and least for the methoxide. This is illustrated by the following table, in which the time in minutes which elapses before one half the active substance has been decomposed is given in each case.

	$C_2H_5 \cdot ONa$.	$C_3H_7 \cdot ONa$.	$CH_3 \cdot ONa$.
CH_3I	16	17	65
C_2H_5I	194	235	410
C_3H_7I	556	752	1053

In the case of the ethoxide, isopropyl iodide was also examined, and the coefficient found to be much lower than that of the normal compound.

In the latter part of the paper, methods of determining the relation between two affinity coefficients and the values of the coefficients from this relation are discussed. H. C.

Determination of the Affinity of Organic Bases. By J. Walker (*Zeit. physikal. Chem.*, **4**, 319—343).—The author attempted to measure the affinities of the organic bases by studying the influence of their hydrochlorides in accelerating the decomposition of methyl acetate by water. Since the acceleration depends on the amount of free acid in solution, the amount of dissociation of the hydrochloride, and from this the relative affinity of the base for the acid, might be thus calculated. The results obtained were not, however, satisfactory except in the case of very feeble bases. The electrical conductivity was therefore resorted to, and from the conductivities of solutions of equal quantities of acid treated with equal quantities of different bases, the amount of salt formed in each, and from this the affinity of the different bases for the acid was deduced. Both sulphuric and hydrochloric acids were found to give good results by this method; and the results thus obtained for feeble bases agree with those obtained by the method first employed.

The dependence of the affinity of organic bases on constitution is to some extent rendered evident by the results. If methyl or ethyl is substituted for the hydrogen of an amido-group, the compound gains in basic properties. The same thing is also true in the case of the substitution of methyl for hydrogen in the carbon-ring of an aromatic base. On the contrary, the substitution of chlorine or a nitro-group for hydrogen in the carbon-ring considerably decreases the basic character of aniline, this effect being greatest in the ortho- and least in the para-position. H. C.

Apparatus for Evaporating by the Aid of Heat applied from above. By W. Hempel (*Ber.*, **22**, 2479—2481).—The author describes, with the aid of a diagram, an apparatus in which small quantities of a liquid can be evaporated by the aid of heat applied from above.

The source of heat is a large, inverted Argand burner, made either entirely of porcelain, or of steatite and metal cemented together with a mixture of soluble glass and finely-divided manganese dioxide. Through the centre of the burner passes a porcelain tube, the lower extremity of which projects a short distance through the flame, the upper extremity being connected with a glass chimney. The crucible or other vessel which contains the substance to be evaporated is placed on a piece of asbestos supported on a moveable iron plate. An inverted beaker, perforated with an aperture just large enough to admit the Argand burner, surrounds the vessel and serves to regulate the supply of heat; if the liquid is evaporated in a basin the employment of the beaker cover is unnecessary.

Clays or fluorides are readily dissolved by the aid of this apparatus. F. S. K.

Inorganic Chemistry.

Preparation of Chlorine in a Kipp's Apparatus. By J. THIELE (*Annalen*, 253, 239—242).—Chlorine may be conveniently prepared in a Kipp's apparatus by the action of hydrochloric acid on bleaching powder. By means of a handpress, the bleaching powder is compressed into a hard cake; this is broken into small lumps and used in this form.

W. C. W.

Automatic Apparatus for Evolving Gases from Liquids. By J. THIELE (*Annalen*, 253, 242—246).—A convenient apparatus for preparing hydrogen chloride from commercial hydrochloric acid or sulphurous anhydride from a concentrated solution of sodium hydrogen sulphite may be made from a three-necked Wolff's bottle. This is provided with—(1) a delivery tube fitted with a stop-cock; (2) a small stoppered separating funnel with the stem drawn out to a fine point; and (3) a safety funnel with some mercury in the bend and a loose plug of cotton wool in the funnel. The Wolff's bottle is half filled with the solution of sodium hydrogen sulphite, for example, and the sulphuric acid is slowly introduced through the separating funnel.

W. C. W.

Reciprocal Displacement of Oxygen and the Halogens. By BERTHELOT (*Compt. rend.*, 109, 546—548 and 590—597).—The author summarises his previous work on the reciprocal displacement of oxygen and chlorine and describes some later results.

Pure concentrated fuming hydrochloric acid is not decomposed by oxygen in presence of sunlight, but if some manganous chloride is present the liquid acquires a deep-brown colour, the atmosphere in the flask becomes charged with chlorine, and the liquid has bleaching properties. Oxygen is absorbed and hydrochlorides of manganese perchloride are formed. If the liberated chlorine is removed and hydrogen chloride and oxygen are introduced into the flask, a further quantity of chlorine is set free, and this process may be repeated several times. The decomposition ceases when the hydrates of the hydrochloric acid contain the maximum amount of water; dilute non-fuming hydrochloric acid is not decomposed even after long exposure in presence of manganese chloride. Ferric chloride behaves in the same manner as manganous chloride, but the phenomena are very much less distinct.

The heat of formation of dissolved hydrobromic acid is almost identical with that of water, and hence in presence of water, but under these conditions only, reciprocal decomposition may take place. In presence of excess of water, oxygen readily decomposes hydrogen bromide under the influence of light. Similar decomposition takes place at the ordinary temperature in the case of a fuming solution of hydrobromic acid, that is, hydrates of the free acid not saturated with water, but is arrested almost immediately by the formation of hydrogen perbrom-

ide, HBr_3; HBr conc. soln. + Br_2 gas = HBr_3 diss. develops +9·2 Cals., the total heat of formation, +43·5 Cals., being greater than the heat of formation of water. Oxygen does not decompose dilute hydrobromic acid, that is, the saturated hydrates of the acid, nor a solution of potassium bromide acidified with hydrochloric acid.

The formation of hydrogen perbromide explains the decomposition of water by bromine, but this change is limited by the dissociation of the perbromide in presence of water.

Dilute solutions of hydriodic acid are readily decomposed by oxygen under the influence of light at the ordinary temperature, the change corresponding with the liberation of 15·9 Cals. for each atom of gaseous iodine.

The heats of formation of dissolved potassium iodide and hydroxide are practically the same, and slight variations in the conditions serve to turn the reaction in one direction or the other. The combination of iodine with potassium iodide in concentrated solution to form potassium triiodide liberates +5·0 Cals. for each atom of gaseous iodine; the action of iodine on dissolved potassium hydroxide with formation of hypoiodite or iodate liberates +4·1 Cals. and +5·4 Cals. respectively for each atom of gaseous iodine. It follows that oxygen will not displace iodine from potassium iodide except under conditions in which potassium triiodide is stable, that is, in very concentrated solutions. Experiment showed that dilute solutions of potassium iodide remain quite colourless when exposed to light for a long time in presence of pure air; very concentrated solutions soon become orange and the colour deepens with prolonged exposure. The liquid then gives a blue coloration with starch and has an alkaline reaction; if, however, it is diluted, it rapidly becomes colourless, owing to dissociation of the potassium triiodide and the action of the liberated iodine on the potassium hydroxide which has been formed.

It is well known that even dilute potassium iodide solutions become yellow when exposed to ordinary air. This is due to the fact that the carbonic anhydride of the air takes part in the reaction. Carbonic acid does not displace hydriodic acid, but the simultaneous action of oxygen and carbonic anhydride on a dilute solution of potassium iodide produces potassium hydrogen carbonate and free iodine, the change being accompanied by the liberation of +13·5 Cals. for each atom of gaseous iodine. The colour of the liquid becomes deeper if the quantity of carbonic anhydride in the atmosphere above it is increased. The action of the oxygen is still greater in presence of acetic or hydrochloric acid, but in these cases the result is in part due to the displacement of some hydriodic acid. Acetic acid liberates very little hydriodic acid, but the action of the oxygen depends on the successive liberation of small quantities. Hydrochloric acid liberates more hydriodic acid and in this case the action of the oxygen is more marked. In presence of a large excess of air, a solution of potassium iodide acidified with hydrochloric acid is completely decomposed by the action of light in a few days.

If manganous chloride is added to a highly concentrated solution of

potassium iodide and the mixture exposed to light, a higher oxide of manganese is precipitated and iodine is liberated; dilute solutions show the same phenomena in a lower degree.

All the reciprocal displacements of oxygen and the halogens under the influence of light are in agreement with the thermochemical determinations. C. H. B.

Simultaneous Synthesis of Water and Hydrogen Chloride. By P. HAUTEFEUILLE and J. MARGOTTET (*Compt. rend.*, **109**, 641—644). —Mixtures which contained oxygen and hydrogen in the proportion required to form water, with varying proportions of chlorine; and mixtures of hydrogen and chlorine in the proportions to form hydrogen chloride, with varying quantities of oxygen, were exploded by means of a spark, and the residual chlorine was determined by means of standard sodium arsenite. If p represents the total hydrogen which enters into combination, and p' the quantity which combines with oxygen, $\frac{p - p'}{p'}$ gives the ratio of the hydrogen converted into water to the hydrogen which forms hydrogen chloride. This ratio is independent of the initial pressure, and of the nature of the spark. It is always less than unity if the proportion of chlorine is more than half the volume of the hydrogen, and it varies with every alteration in the proportion of chlorine. When the volume of chlorine present is double the volume of the hydrogen, the quantity of water formed becomes inappreciable. It is evident that the results do not agree with Bunsen's law.

With equal volumes of hydrogen and chlorine and varying proportions of oxygen, the ratio $\frac{p - p'}{p}$ is always less than unity and does not vary greatly when the ratio of oxygen to hydrogen varies from 0·25 to 3. With equal volumes of the three gases the change is represented by the equation $5Cl_2 + 5H_2 + 5O_2 = 8HCl + H_2O + Cl_2 + 4O_2$. C. H. B.

Equilibrium between Hydrogen, Chlorine, and Oxygen. By H. LE CHATELIER (*Compt. rend.*, **109**, 664—667).—The author discusses the results of Hautefeuille and Margottet (preceding Abstract) from the point of view of his own laws of chemical equilibrium. The agreement between the observed and calculated numbers is very close. He points out that the degree of moisture of the gases, which is very important, is not specified. The formula shows that a reduction of initial pressure should be accompanied by a reduction in the proportion of water formed, and the fact that this is not observed indicates that the chlorine is partially dissociated. The varying effects of chlorine and oxygen depend solely on their relative volumes and not on their chemical properties. C. H. B.

Preparation of Oxygen in a Kipp's Apparatus. By J. VOLHARD (*Annalen*, **253**, 246—248).—Small quantities of oxygen can be conveniently prepared in a Kipp's apparatus by the action of hydrogen

peroxide on bleaching powder. Nitric acid is added in sufficient quantity to neutralise the lime in the bleaching powder. The oxygen contains a small quantity of chlorine. W. C. W.

Action of Sulphur on Solutions of Metallic Salts. By G. VORTMANN and C. PADBERG (*Ber.*, **22**, 2642—2644).—The authors find that with many proto-salts when their aqueous solutions are boiled with flowers of sulphur, about half the metal present is precipitated as sulphide, the remainder being oxidised to the per-salt. When a strongly acid solution of stannous chloride was employed, no stannous sulphide was precipitated, but hydrogen sulphide was evolved, and the whole of the tin oxidised to stannic chloride. With an aqueous solution of stannous chloride, and with an acid solution of cuprous chloride, rather less than half the tin was precipitated as sulphide, a little being oxidised in the same manner as with the strongly acid solution of tin. With mercurous nitrate, almost exactly half of the mercury was precipitated as sulphide.

Solutions of manganese, iron, nickel, zinc, and cadmium sulphates, and acid solutions of bismuth and antimonious chlorides, and of arsenious and arsenic acids, are not altered when boiled with sulphur. L. T. T.

Preparation of Nitric Oxide. By J. THIELE (*Annalen*, **253**, 246).—Nitric oxide is prepared in the apparatus previously described (this vol., p. 6) by adding a strong solution of sodium nitrite to a solution of ferrous chloride or sulphate in hydrochloric acid. If the sodium nitrite contains carbonate, it may be removed by precipitation with calcium chloride. W. C. W.

Phosphonium Sulphate. By A. BESSON (*Compt. rend.*, **109**, 644—645).—When hydrogen phosphide is passed into sulphuric acid at the ordinary temperature, there is considerable development of heat, sulphur separates, and sulphurous acid is formed. If the acid is previously cooled by means of ice and salt, the gas is somewhat largely absorbed, and the liquid remains limpid. After a time, however, it begins to decompose in the manner indicated, the temperature rises, and decomposition becomes very rapid. If the acid is cooled to $-20°$ or $-25°$ by the rapid evaporation of methyl chloride, a syrupy liquid is obtained, from which a white, crystalline, highly deliquescent, solid separates; this seems to be phosphonium sulphate. When thrown into water at the ordinary temperature, it dissolves with a strident noise, and hydrogen phosphide is evolved, but the sulphuric acid is not reduced. When exposed to air at the ordinary temperature, the phosphorus is oxidised to phosphoric, phosphorous, and hypophosphorous acids, whilst the sulphuric acid is reduced to sulphurous acid and sulphur, with a small quantity of hydrogen sulphide. The crystals may be dissolved in dilute sulphuric acid, and if the solution is electrolysed at $-25°$ or $-40°$ with a mercury cathode, there is only a very slight intumescence of the mercury, and hence, if phosphonium amalgam exists, it is very unstable even at the freezing point of mercury. The solution has a high resistance, and if the

current is too strong the compound is decomposed with great rapidity in the manner already described.

Hydrogen phosphide has no action on nitric acid at −25°.

C. H. B.

Behaviour of Sodium Thiosulphate towards Acids and Metallic Salts. By W. VAUBEL (*Ber.*, **22**, 2703—2704).—A reply to Vortman (Abstr., 1889, 1107) upholding the author's previous views (*ibid.*, p. 943).

Direct Production of Crystalline Sodium Carbonate and Chlorine from Sodium Chloride. By W. HEMPEL (*Ber.*, **22**, 2475—2478).—In the electrolysis of metallic chlorides, which give readily soluble decomposition-products, the latter are further decomposed as soon as the quantity produced reaches a certain limit. When, however, the compound produced is only sparingly soluble, this secondary decomposition does not take place, and the whole strength of the current is utilised. Potassium chloride and sodium chloride, for example, can be converted into the corresponding chlorate; calcium chloride and magnesium chloride can be decomposed into chlorine and a solid hydroxide, by employing a diaphragm.

Marx (D. R.-P., No. 46318) has shown that alkaline chlorides can be directly converted into chlorine and an alkaline hydrogen carbonate, by passing carbonic anhydride through the solution during electrolysis, metal and liquid diaphragms being employed.

The author, who has been engaged independently in making similar experiments, describes, with the aid of diagrams, an apparatus in which sodium chloride can be directly converted into chlorine and crystalline carbonate. The cathode is a perforated iron disc, the anode a perforated carbon disc, the perforations being about 4 mm. in diameter, and bored in an upward direction to allow the gas to escape freely. A disc of ordinary asbestos-paper, placed immediately between the carbon and iron discs, serves as a diaphragm. The three discs are placed in the centre of a vessel made of porcelain and glass, which is thus divided into two chambers, each of which is provided with a conducting tube, in one case for carbonic anhydride, in the other for chlorine. If sodium chloride is added from time to time through a suitable aperture, and the water which is removed with the crystalline carbonate is replaced, the apparatus can be worked continuously, sodium carbonate and almost chemically pure chlorine being obtained.

A tension of 3·2 volts is required for decomposing the sodium chloride, and a tension of 2·5 volts to overcome the polarisation current; but the latter has only a slight tension when both electrodes are made of carbon. With a current of 1·73 ampères 0·93 gram of chlorine per hour was produced, so that if a dynamo were employed it should give 64·5 grams of chlorine and 259·8 grams of $Na_2CO_3 + 10H_2O$ per horse-power-hour.

F. S. K.

Preparation of Crystalline Normal Lithium Phosphate and Arsenate. By A. DE SCHULTEN (*Bull. Soc. Chim.* [3], **1**, 479—480).—Fused lithium chloride dissolves the amorphous, normal phosphate, and on cooling and washing the melt, rhomboidal, tabular crystals of

normal lithium phosphate, which have a sp. gr. 2·41 at 15°, and are infusible at a white heat, are obtained.

The normal arsenate is similarly prepared; it corresponds with the phosphate physically, and is of sp. gr. 3·07 at 15°. T. G. N.

Cadmium Phosphates and Arsenates. By A. DE SCHULTEN (*Bull. Soc. Chim.* [3], **1**, 473—479).—The normal orthophosphate, $Cd_3(PO_4)_2$, falls as a voluminous, amorphous precipitate when normal sodium phosphate is added to the solution of a cadmium salt.

Hydrogen disodium phosphate throws down from a hot solution of cadmium chloride or sulphate an amorphous precipitate which quickly becomes crystalline. After purification by dissolution in phosphoric acid and cautious reprecipitation by alkaline hydroxides, it forms small, prismatic hexagons of sp. gr. 3·98 at 15°, having the composition $H_2Cd_5(PO_4)_4 + 4H_2O$; these, when dissolved in cold phosphoric acid (sp. gr. 1·1), are reprecipitated unaltered on warming or on heating in sealed tubes to 250°, but redissolve on cooling; as thus produced, their sp. gr. is 4·12 at 15°. This phosphate loses its water at a red heat, and fuses at a white heat; it is probably the compound described by Stromeyer as the normal phosphate.

Monocadmium phosphate, $H_4Cd(PO_4)_2 + 2H_2O$, crystallises out after slow evaporation of a saturated solution of the previous salt in cold dilute phosphoric acid at the normal temperature. It exists as large clino-rhombic prisms of sp. gr. 2·742 at 15°, which lose their water of crystallisation at 100°, and are decomposed by water to form a flocculent phosphate, $H_2Cd_5(PO_4)_4 + 4H_2O$.

Cadmium chlorapatite.—Normal cadmium orthophosphate and the second phosphate described above dissolve in fused cadmium chloride, and on slowly cooling the melt, long, hexagonal prisms of the salt, $3Cd_3(PO_4)_2,CdCl_2$, of sp. gr. 5·46 at 15°, separate.

A cadmium bromapatite, $3Cd_3(PO_4)_2,CdBr_2$, may be similarly prepared, but is always contaminated with cadmium pyrophosphate, from which it may be separated by cold, dilute nitric acid, which dissolves only the bromapatite; the cadmium pyrophosphate, $Cd_2P_2O_7$, exists as flattened oblique lamellæ of sp. gr. 4·965 at 15°.

Cadmium arsenates.—When the amorphous powder, $H_2Cd_5(AsO_4)_4 + 4H_2O$, which is precipitated on the addition of hydrogen disodium arsenate to the solution of a cadmium salt, is dissolved to saturation in a cold solution of arsenic acid of sp. gr. 1·3, and, subjected to heat, crystals of the salt $HCdAsO_4 + H_2O$, having a sp. gr. of 4·164 at 15° are deposited.

Monocadmium arsenate, $H_4Cd(AsO_4)_2 + 2H_2O$, crystallises out when a saturated solution of the compound $H_2Cd_5(PO_4)_4 + 4H_2O$, in arsenic acid solution (sp. gr. 1·3), is allowed to evaporate at the ordinary temperature. It forms large, clino-rhombic prisms of sp. gr. 3·241 at 15°, which are isomorphous with those of the corresponding phosphate. At 70—80°, they lose their water of hydration, and are partly decomposed; with excess of water, they form a flocculent substance, $H_2Cd_5(AsO_4)_4 + 4H_2O$.

Cadmium chlorarsenioapatite, $3Cd_3(AsO_4)_2,CdCl_2$, is produced by fusing either normal ammonium arsenate or the salt $H_2Cd_5(AsO_4)_4$ +

$4H_2O$, with excess of cadmium chloride. Its sp. gr. is 5·865 at 15°, and its physical properties correspond with those of the chlorapatite.

Cadmium bromarsenioapatite, $3Cd_3(AsO_4)_2,CdBr_2$. is similarly prepared, and exists as long yellow prisms of sp. gr. 6·017.

Cadmium pyroarsenate, $Cd_2As_2O_7$, is prepared by fusing a mixture of cadmium bromide (22 parts) with potassium bromide (5 parts), and adding to the fused mass normal ammonium arsenate (9 parts); after washing the melt, the colourless crystals of the pyroarsenate are separated from the yellow bromarsenioapatite by treatment with dilute nitric acid, which dissolves the latter compound only. This pyroarsenate forms crystals of sp. gr. 5·474 at 15°, corresponding in physical properties with the pyrophosphate. T. G. N.

Action of Sodium Thiosulphate on Metallic Salts. By G. VORTMANN and C. PADBERG (*Ber.*, **22**, 2637—2641).—The authors have extended Vortmann's work on copper salts (Abstr., 1888, 787) to other metallic salts.

When a concentrated solution of sodium thiosulphate is added to a strong solution of lead acetate until the lead thiosulphate first precipitated has been just redissolved, and alcohol is then added, an oily liquid separates, which when rubbed with absolute alcohol solidifies to a crystalline mass of the formula $PbS_2O_3,3Na_2S_2O_3 + 12H_2O$.

Thallious sulphate under similar treatment yields small needles of the formula $Tl_2S_2O_3,2Na_2S_2O_3 + 8H_2O$.

When molecular proportions of cadmium sulphate and barium thiosulphate are rubbed together with a little water, the insoluble barium sulphate formed filtered off, and alcohol added to the filtrate, *cadmium thiosulphate*, $CdS_2O_3 + 2H_2O$, separates as an oil, which gradually solidifies to a yellowish-white, crystalline mass. When equal molecular proportions of sodium thiosulphate and cadmium nitrate in aqueous solution are mixed together and alcohol added, yellowish-white needles of the formula $2CdS_2O_3,Na_2S_2O_3 + 7H_2O$ are formed. If a large excess of the thiosulphate is used, the compound $CdS_2O_3.3Na_2S_2O_3 + 9H_2O$ separates as an oil. This gradually solidifies to small, yellow scales, which lose 4 mols. H_2O over sulphuric acid.

On mixing strong solutions of zinc iodide and sodium thiosulphate and adding alcohol, an oil separates, which after long exposure over sulphuric acid solidifies to a gum-like mass of the formula $2ZnS_2O_3,3Na_2S_2O_3 + 10H_2O$. It is deliquescent, and decomposes gradually with formation of zinc sulphide.

Ferrous thiosulphate, $FeS_2O_3 + 5H_2O$, forms green crystals easily soluble in water. A double salt, $FeS_2O_3,3Na_2S_2O_3 + 8H_2O$, was obtained by precipitating a mixed solution of ferrous iodide and sodium thiosulphate with alcohol. It forms bright-green crystals, soluble in water.

Manganese thiosulphate, $MnS_2O_3 + 5H_2O$, is crystalline but unstable. A pale, rose-coloured double salt, $MnS_2O_3,2Na_2S_2O_3 + 16H_2O$, was obtained.

The cobalt double salt, $CoS_2O_3,3Na_2S_2O_3 + 15H_2O$, forms a blue,

gum-like mass, soluble in water. No corresponding nickel salt could be prepared, though a crystalline salt, $NiS_2O_3,6NH_3,3H_2O$, was obtained. L. T. T.

New Method of Preparing Anhydrous Aluminium Chloride. By C. F. MABERY (*Ber.*, **22**, 2658).—The author finds that dry hydrogen chloride extracts the whole of the aluminium from an alloy of copper and aluminium without attacking the copper. The reaction is most energetic a little below a red heat. The alloys containing 15 to 40 per cent. of aluminium are best powdered, mixed with powdered charcoal (to prevent the fusion of the remaining copper), put into a graphite retort, and when heated just below a red heat a current of hydrogen chloride is passed through. The aluminium chloride distils over, and may be condensed in suitable vessels, the liberated hydrogen passing on. L. T. T.

Alkali Aluminium Silicates. By A. GORGEU *Zeit. Kryst. Min.*, **15**, 646, from *Bull. soc. fran. min.*, **10**, 278).—On melting kaolin with alkali haloid salts in the presence of moist air, silicates are formed, having the composition $AlR'SiO_4$. By melting kaolin with potassium carbonate or caustic potash at a dull-red heat, an amorphous salt, $AlKSiO_4$, is obtained, whilst at a more intense heat octahedra are obtained, having the composition $Al_2K_2SiO_6$, or else a more basic silicate also crystallising in the regular system. The sodium-compounds prepared in a similar way are always basic, and form doubly refracting crystals. B. H. B.

Mercuricobaltammonium Salts. By G. VORTMANN and E. MORGULIS (*Ber.*, **22**, 2644—2648).—When solutions of the mercuric double salts of cobaltammonium chlorides are treated with potash or soda, red precipitates are formed, which appear to be cobalt-ammonium chlorides, in which part of the hydrogen is replaced by varying proportions of the univalent radicles (HgCl) or (HgOH).

Luteocobalt salts. A solution of the salt $Co_2(NH_3)_{12}Cl_6,6HgCl_2$, or a mixture of one part by weight of luteocobalt chloride and three parts of mercuric chloride, when treated with 6 mols. of soda yields the salt $Co_2N_{12}H_{28}(HgCl)_6(HgOH)_2Cl_6$; or with excess of soda, the salt $Co_2N_{12}H_{28}(HgOH)_8Cl_6$. Both compounds are bright-red, and decompose quickly when moist, slowly when dry. Equal weights of luteocobalt chloride and mercuric chloride with excess of soda yield a slightly more stable, red salt, $Co_2N_{12}H_{32}(HgOH)_4Cl_6$.

Purpureocobaltdecamine salts.—1 mol. of purpureocobalt chloride, 6 mols. of mercuric chloride, and 6 mols. of soda yield a dark-red, flocculent salt, $Co_2N_{10}H_{22}(HgCl)_6(HgOH)_2Cl_6$; with excess of soda, the salt $Co_2N_{10}H_{22}(HgOH)_8Cl_6$ is formed.

Roseocobaltdecamine salts.—1 mol. of roseocobalt chloride, 6 mols. of mercuric chloride, and 6 mols. of soda yield a violet-red precipitate, $Co_2N_{10}H_{21}(HgOH)_6Cl_6$; with excess of soda, a salt,

$$Co_2N_{10}H_{24}(HgOH)_6Cl_4(OH)_2,$$

is formed. Both salts are very unstable.

Purpureocobaltoctamine salts.—1 mol. of purpureocobaltoctamine chloride, 6 mols. of mercuric chloride, and 6 mols. of soda yield the salt, $Co_2N_8H_{16}(HgCl)_4(HgOH)_4Cl_6$; with excess of soda, the salt $Co_2N_8H_{16}(HgOH)_8Cl_6$ is formed.

Equal weights of the cobalt and mercuric salts with excess of soda yield the salt $Co_2N_8H_{16}(HgOH)_8Cl_4(OH)_2$.

Roseocobaltoctamine salts.—Under like conditions as with the purpureo-salts, the three salts, $Co_2N_8H_{16}(HgCl)_6(HgOH)_2Cl_6$,

$$Co_2N_8H_{16}(HgOH)_8Cl_6,$$

and $Co_2N_8H_{16}(HgOH)_8Cl_4(OH)_2$, are formed. All three are violet-red, and decompose at ordinary atmospheric temperature, as do also the corresponding purpureo-compounds. L. T. T.

Cobaltoctamine Salts. By G. VORTMANN and O. BLASBERG (*Ber.*, **22**, 2648—2655).—When cobalt nitrate, sulphate, or chloride is dissolved in a small quantity of water and added to a mixture of ammonia and ammonium carbonate, violet-red solutions are formed. If these are oxidised by a current of air, decamine salts are formed, but on evaporation these are decomposed, octamine salts crystallising out. The following salts are described:—

$Co_2(NH_3)_{10}(NO_3)_2(CO_3)_2,2H_2O$	Crystalline.
$Co_2(NH_3)_{10}(SO_4)_2CO_3,4H_2O$	Crystalline.
$Co_2(NH_3)_8(NO_3)_2(CO_3)_2,H_2O$	Cherry red crystals.
$Co_2(NH_3)_8(SO_4)_2CO_3,4H_2O$	Long, thin needles.
$Co_2(NH_3)_8SO_4(CO_3)_2,3H_2O$	Dark red, prismatic crystals.
$Co_2(NH_3)_8Cl_4CO_3,2H_2O$	Crystalline.
$Co_2(NH_3)_8Cl_2(CO_3)_2,H_2O$	,,
$Co_2(NH_3)_8(NO_3)_2(SO_4)_2,2H_2O$	,,
$Co_2(NH_3)_8(NO_3)_6,2H_2O$	,,
$Co_2(NH_3)_8(NO_3)_2Cl_4,4H_2O$	,,
$Co_2(NH_3)_8(NO_3)_2I_4,2H_2O$	,,
$Co_2(NH_3)_8Br_2(SO_4)_2$	,,
$Co_2(NH_3)_8I_2(SO_4)_2$	,,
$Co_2(NH_3)_8I_2Cl_4,2H_2O$	Brown scales.
$Co_2(NH_3)_8(OH)_2Cl_4,2H_2O$	Dark green powder.
$Co_2(NH_3)_8(OH)_2Cl_4,2HgCl_2$	
$Co_2(NH_3)_8(OH)_2Cl_4,PtCl_4,H_2O$	

L. T. T.

Action of Sulphurous Acid on Cobaltammonium Salts. By G. VORTMANN and G. MAGDEBURG (*Ber.*, **22**, 2630—2637).—The authors have obtained the following compounds:—

$Co_2(NH_3)_8(SO_3Am)_6,10H_2O$	Yellowish-brown needles.
$Co_2(NH_3)_8(SO_3)_6Ba_3,7H_2O$	Golden-yellow scales.
$Co_2(NH_3)_8(SO_3)_6Ba_2Am_2,7H_2O$	Golden-yellow scales.
$Co_2(NH_3)_8(SO_3)_6Co_2^{vi},36H_2O$	Orange crystals.
$Co_2(NH_3)_8(SO_3)_6Co_2^{vi},24H_2O$	Orange crystals.

$Co_2(NH_3)_8(SO_3)_6(NH_3)_{12}Co_2^{vi}.8H_2O$ ..	Orange powder.
$Co_2(NH_3)_6(SO_3)_2(SO_3Am)_2,4H_2O$.....	Yellowish-brown needles.
$Co_2(NH_3)_8SO_4(SO_3)_4Co_2^{vi},24H_2O$	Yellow crystalline powder.
$Co_2(NH_3)(NH_3)_8(SO_3)_2Cl_2,4H_2O$	Dark brown crystals.
$Co_2(NH_3)_{10}(SO_3Na)_6,2H_2O$	Light brown crystals.
*$Co_2(NH_3)_{10}(SO_3)_6Co_2^{vi},8H_2O$	Brownish-yellow powder.
$Co_2(NH_3)_{10}(SO_3)_3,3H_2O$.............	
$Co_2(NH_3)_{10}(SO_3)_2Cl_2$................	Brown crystalline powder.
$Co_2(NH_3)_{12}(SO_3)_2Cl_2,6H_2O$	Yellow needles.

The authors consider that these salts show the existence of four series of salts.

1. $Co_2(NH_3)_{6-12}(SO_3)_3$.
2. $Co_2(NH_3)_{6-12}(SO_3)_2(SO_3R)_2$.
3. $Co_2(NH_3)_{6-12}(SO_3)(SO_3R)_4$.
4. $Co_2(NH_3)_{6-12}(SO_3R)_6$.

L. T. T.

New case of Isomorphism of Uranium and Thorium. By C. RAMMELSBERG (*Zeit. Kryst. Min.*, **15**, 640—641; from *Sitzber. preuss. Akad. Wiss.*, 1886, 603).—The author shows that the thorium sulphate described by Nordenskiöld and others, and the uranium sulphate hitherto regarded as rhombic, have a similar composition, namely:—

$$(SO_4)_2Th + 9H_2O,$$
$$(SO_4)_2U + 9H_2O.$$

The crystals of the latter are only seemingly rhombic in consequence of twin-formation; in reality they are monosymmetric, like the thorium sulphate. The axial ratios of the two minerals are: uranium sulphate, $a : b : c = 0{\cdot}597 : 1 : 0{\cdot}6555$, $\beta = 82° 11'$; thorium sulphate, $a : b : c = 0{\cdot}598 : 1 : 0{\cdot}658$, $\beta = 81° 50'$. B. H. B.

Fluorine-compounds of Vanadium and its Analogues. By E. PETERSEN (*J. pr. Chem.* [2], **40**, 271—296; compare Abstr., 1889, 107).—The following double salts of vanadium oxyfluorides and potassium fluoride have been obtained:—

$2KF,VOF_3$, a white, crystalline precipitate, is obtained by adding a solution of potassium fluoride to one of vanadic acid in hydrofluoric acid; when dried over sulphuric acid, it becomes reddish-brown, and has the above formula.

$4KF.VF_5,VOF_3$ separates as a white precipitate from the mother-liquor of the above salt.

$HF,3KF,2VOF_3$ crystallises from a hot solution of either of the preceding salts in hydrofluoric acid in beautiful, colourless prisms, which lose very little weight at 100°.

$3KF,VOF_3,VO_2F$ is the white, crystalline residue left when the precipitate obtained by adding a solution of vanadium pentoxide in hydrofluoric acid to a solution of potassium fluoride is treated with water at the ordinary temperature; if hot water is used and the solution is poured into a hot solution of potassium fluoride, a crystalline precipitate is obtained, of uncertain composition, but approaching

* Probably Künzel's pentaminedicobaltic sulphite.

the formula $4KF,VOF_3,VO_2F$; or if the first-mentioned precipitate is heated with water for some minutes, a salt having nearly the composition VOF_3,VO_2F is obtained.

$2KF,VO_2F$ separates from a warm solution of vanadium pentoxide in hydrofluoric acid when it is nearly neutralised with potassium hydroxide. It crystallises in yellow, six-sided, truncated prisms. When recrystallised from water, it yields the salt $3KF,2VO_2F$.

$3HF,9NH_4F,5VOF_3$, obtained by adding ammonium fluoride in slight excess to the solution of vanadium pentoxide in hydrofluoric acid, crystallises in large, colourless, four-sided prisms.

$3NH_4F,VO_2F$ crystallises from a solution of vanadium pentoxide in hydrofluoric acid when it is nearly neutralised with ammonia. The crystallography of the salt is given.

$HF,7NH_4F,4VO_2F$ separates in white crystals from the solution of the last-named salt in warm water.

$2Nb_2O_5,3KF,5H_2O$ is obtained by melting niobium pentoxide (1 part) with potassium fluoride (3 25 parts) and treating the melt with water, when the salt remains undissolved as a crystalline powder.

$Nb_2O_5,KF,3H_2O$ is a prismatic, crystalline powder, obtained by fusing niobium pentoxide (1 part) with potassium fluoride (1·3—1·5 parts).

The author reviews the work already done on the vanadium double fluorides, and concludes his paper with the following directions for extracting vanadic acid from the finery slag of Taberg:—300 grams of the finely-powdered slag is mixed with 400 c.c. of hydrochloric acid (sp. gr. 1·18) and shaken. After 24 hours, water is added to make the bulk up to $1\frac{1}{2}$ litres, and the whole filtered through linen. Iron is then added, and, after the evolution of hydrogen has ceased, sodium acetate until the liquid is reddish-brown; finally, acetic acid and sodium phosphate are added until all iron, chromium, aluminium, and vanadium are precipitated as phosphates. The precipitate is mixed with sodium carbonate (0·5 part) and heated on an iron plate for $\frac{1}{2}$—$\frac{3}{4}$ hour; the mass is treated with water, hydrochloric acid added to nearly neutralise the solution, which is then heated, filtered, and made acid with acetic acid; solid ammonium chloride is now added, when a red, crystalline ammonium vanadate, $(NH_4)_2O.2V_2O_5,4H_2O$, separates; this is heated and the residual vanadium oxide treated with hot nitric acid at 110—120°, and converted into ammonium metavanadate by evaporating off the nitric acid, dissolving in ammonia, and crystallising; pure vanadic acid is obtained from this salt by igniting and repeating the nitric acid treatment. A. G. B.

Vapour-density of Antimony Pentachloride. By R. Anschütz and N. P. Evans (*Annalen*, **253**, 95—105).—By means of a modification of La Coste's apparatus, the authors have attempted to determine the density of the vapour of antimony pentachloride under reduced pressure. As antimony trichloride boils at 143—144° under 70 mm. pressure and antimony pentachloride boils at 102—103° under 68 mm. pressure, the determinations were made under 58 mm. pressure at a temperature of 218°. The mean of four determinations gave the value 10, the theoretical density being 10·33. It was impossible to

exclude all traces of moisture from the apparatus and avoid the formation of minute quantities of the monohydrate of antimony pentachloride.

W. C. W.

Atomic Weight of Palladium. By E. H. KEISER (*Amer. Chem. J.*, **11**, 398—403).—Attempts were at first made to use the double chlorides of palladium with ammonium and with sodium, but they had to be abandoned, as these compounds contain water, from which it is almost impossible to completely free them; moreover, the dried salts are very hygroscopic, and absorb water rapidly while being weighed.

Finally, the yellow, crystalline palladiodiammonium chloride, $PdN_2H_6Cl_2$, was used; this is formed whenever hydrochloric acid is added to a solution of palladium chloride in excess of ammonia; it is a stable compound, and can be obtained very pure. It contains no water of crystallisation, can be dried completely, and is not hygroscopic. When heated in a current of pure hydrogen, the colour changes from yellow to black, hydrogen being absorbed, and metallic palladium and ammonium chloride formed. On raising the temperature, the ammonium chloride volatilises, and spongy palladium is left behind; this is cooled below a red heat in a current of hydrogen, and then the hydrogen is displaced by air; in this way the occlusion of hydrogen is prevented. The weight of palladium obtained from a known weight of the chloride is thus ascertained, and from this the atomic weight of palladium is calculated, assuming N = 14·01, H = 1, Cl = 35·37. Two series of experiments were made; the palladammonium chloride used in the second series was prepared from the metallic palladium obtained in the first. The results give as mean value Pd = 106·35:—

		Atomic weight.		
Series.	Experiments.	Mean.	Maximum.	Minimum.
I.	11	106·352	106·459	106·292
II.	8	106·350	106·455	106·286

C. F. B.

Ruthenium Potassium Nitrites. By A. JOLY and M. VÈZES (*Compt. rend.*, **109**, 667—670; compare Abstr., 1889, p. 352).—If ruthenium chloride is added to a boiling solution of potassium nitrite until the precipitate which forms at first is redissolved, and the liquid is concentrated and allowed to cool, it deposits dichroic, orange-red, monoclinic prisms of 90° 10′. They are very soluble in water, can be purified by repeated recrystallisation without undergoing alteration, and have the composition $Ru_2O_2(N_2O_3)_4,4KNO_2$ or $Ru_2O_3(NO)_2,(N_2O_3)_2,4KNO_2$.

When the potassium nitrite is in excess, and prolonged ebullition is avoided, a pale-yellow, crystalline precipitate is obtained of the composition $Ru_2O_2,(N_2O_3)_2,8KNO_2$ or $Ru_2O_3(NO)_2,N_2O_3,8KNO_2$. Separation of the ruthenium is never complete, and the mother-liquor, on concentration, yields crystals of the first compound. The second salt is converted into the first by prolonged ebullition with water, and the reverse change is effected by the addition of potassium nitrite. At a

low temperature, the second salt crystallises with 2 mols. H_2O. Other double nitrites seem to be formed, but are relatively very unstable.

If the double nitrites are heated with ammonium chloride and hydrochloric acid, only part of the nitrogen is evolved and one atom of the nitrogen remains in combination with each atom of ruthenium. The solution when concentrated yields the potassium ruthenium nitrosochloride previously described (*loc. cit.*).

No compound was obtained corresponding with that to which Claus attributes the formula $Ru(NO_2)_3,3KNO_2$. C. H. B.

Mineralogical Chemistry.

Glaserite from Douglashall. By H. BÜCKING (*Zeit. Kryst. Min.*, **15**, 561—575).—In the astrakanite (bloedite) of Douglashall, crystals of potassium sodium sulphate have recently been found. The crystals vary from 5 to 20 mm. in length. They have a hardness of $2\frac{3}{4}$ to 3, and a sp. gr. of 2·650 to 2·656, the differences being due to small inclusions of rock-salt. The crystals belong to the hexagonal system, the axial ratio being $a : c = 1 : 1·2879$. These samples of crystals, easily soluble in water, gave on analysis the following results:—

	K_2SO_4.	Na_2SO_4.	$MgSO_4$.	NaCl.	Insol.	H_2O and loss.	Total.
I.	66·5	22·0	—	10·1	0·4	1·0	100·0
II.	67·3	18·2	—	11·6	—	2·9	100·0
III.	58·7	19·5	3·4	14·4	0·1	3·9	100·0

The author also gives crystallographical descriptions of bloedite, kainite, and boracite from the same locality. B. H. B.

Atelestite from Schneeberg, in Saxony. By K. BUSZ (*Zeit. Kryst. Min.*, **15**, 625—627).—A specimen of this rare mineral from the Neuhilfe mine, at Schneeberg, gave on analysis results corresponding with the formula $As_2O_5,3Bi_2O_3,2H_2O$. The axial ratio was calculated by G. v. Rath to be $a : b : c = 0·869 : 1 : 1·822$, $\beta = 110° 30'$; whilst the author finds that it is

$$a : b : c = 0·92974 : 1 : 1·51227. \quad \beta = 110° 25'.$$

The hardness is $3\frac{1}{2}$, and the sp. gr. 6·4. B. H. B.

Artificial Preparation of Wollastonite. By A. GORGEU (*Zeit. Kryst. Min.*, **15**, 646; from *Bull. Soc. fran. min.*, **10**, 271).—One equivalent of $CaCl_2$ melted with one equivalent of precipitated silica, in the presence of steam, gives $CaSiO_3$, whilst two equivalents of the former give Ca_2SiO_4, which, however, cannot be isolated in distinct crystals. With a larger excess of calcium chloride, the compound $Ca_2Cl_2SiO_3$ is obtained in rhombic crystals and pseudo-

hexagonal tablets, whose composition is probably $Ca_2Cl_2SiO_3$. If 1 gram of SiO_2, 15 grams of $CaCl_2$, and 3 grams of NaCl are melted for half an hour in a current of moist air there is obtained, besides small quantities of the chlorides mentioned above and of tridymite, long prisms of wollastonite exhibiting the optical properties of the natural mineral. B. H. B.

Anorthite and Enstatite. By K. v. CHROUSTSCHOFF (*Zeit. Kryst. Min.*, **15**, 649; from *Bull. Soc. fran. min.*, **10**, 329).—The olivine inclusions in the basalt of Wingendorf, in Silesia, contain anorthite (I) and almost colourless enstatite (II). Both minerals were isolated and analysed with the following results:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	Ignition.	Total.
I.	44·68	35·32	0·41	—	1·13	17·45	1·33	0·45	0·33	101·10
II.	56·96	0·79	—	3·11	33·65	4·32	traces		0·26	99·09

B. H. B.

Minerals from Fiskernäs, in Greenland. By N. V. USSING (*Zeit. Kryst. Min.*, **15**, 596—615).—1. *Sapphirine.*—The sapphirine-bearing rock belongs to the crystalline schist series. The sapphirine occurs in blue, tabular crystals, with distinct pleochroism. The axial ratio is calculated to be $a : b : c = 0·65 : 1 : 0·93$. $\beta = 79° 30'$. The hardness of sapphirine is $7\frac{1}{2}$, and its sp. gr. is 3·486. Analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	Ignition.	Total.
12·83	65·29	0·93	0·65	19·78	0·31	99·79

Formula: $Mg_5Al_{12}Si_2O_{27}$.

2. *Kornerupine.*—This was described as a new mineral by Lorenzen. No crystallographical and optical examination has hitherto been made. The mineral belongs to the rhombic system, the axial ratio being $a : b = 0·854 : 1$. Its formula is $MgAl_2SiO_6$. It is perhaps identical with the prismatine of Sauer.

3. *Gedrite.*—This mineral is found at Fiskernäs in colourless grains or short prisms, having a hardness of 5·5 and a sp. gr. of 3·100. Analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	Na_2O.	H_2O.	Total.
46·18	21·78	0·44	2·77	25·05	2·30	1·37	99·89

Formula: $(NaH)_2SiO_3,6MgSiO_3,2Al_2O_3$. This variety of gedrite differs from all other rhombic amphiboles by its high percentage of alumina.

4. *Pargasite.*—This monosymmetric hornblende occurs in small, transparent grains, having a sp. gr. of 3·064, and giving on analysis—

SiO_2.	Al_2O_3.	Cr_2O_3.	FeO.	CaO.	MgO.	Ignition.	Total.
46·79	15·36	0·69	2·38	13·11	20·17	2·13	100·63

B. H. B.

Artificial Fayalite. By A. FIRKET (*Zeit. Kryst. Min.*, **15**, 652—653; from *Ann. Soc. géol. Belg.*, **14**, 196).—A slag from the Ongrée ironworks analysed by the author gave the following results :—

SiO_2.	FeO.	Fe_2O_3.	MnO.	S.	P.	Total.
28·00	62 00	9·30	0·97	0·14	0·50	100·91

The hardness is 6, and the sp. gr. 4·212. B. H. B.

Organic Chemistry.

Tetrabromides of Diallyl. By G. CIAMICIAN and F. ANDERLINI (*Ber.*, **22**, 2497—2500).—A small quantity of an oily bromide, $C_6H_{10}Br_4$, is formed in preparing diallyl tetrabromide (m. p. 63°) by treating the hydrocarbon with bromine; when the crude product is crystallised from alcohol, the liquid bromide remains in solution. It boils at 135—140° (about 8 mm.) with slight decomposition, and its molecular weight, determined by Raoult's method in benzene solution, was found to be 325 as the average of two experiments.

F. S. K.

γ-Pentyleneglycol and its Anhydride (Tetrahydromethylfurfuran). By A. LIPP (*Ber.*, **22**, 2567—2573).—γ-Pentyleneglycol (Freer and Perkin, Trans., 1887, 836) mixes in all proportions with water, alcohol, and chloroform, is rather sparingly soluble in ether in presence of moisture, and is insoluble in light petroleum. At −18°, it is quite viscid. It boils at 219—220° (under 713 mm. pressure), and does not decompose at 236°. Sp. gr. = 1·0003 at 0° (water at 0° = 1). When heated with 35—40 per cent. hydrobromic acid for one hour at 100°, the anhydride is formed; this boils at 77—79°; sp. gr. = 0·8748 at 0° (water at 0° = 1). It is not changed when heated with water at 200—210°. Ammonia is also without action on it at 200°.

γ-Pentylene dibromide, $CHBrMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$, is obtained by heating the glycol or the anhydride with 3 to 4 parts of fuming hydrobromic acid for three hours at 100°. It boils at 200—202° with partial decomposition, is insoluble in water, readily soluble in alcohol, ether, chloroform, and carbon bisulphide. N. H. M.

Action of Lead Peroxide on Organic Substances in Alkaline Solution. By M. GLÄSER and T. MORAWSKI (*Monatsh.*, **10**, 578—584).—When a mixture of glycerol (2 grams), sodium or potassium hydroxide (5—10 grams), and lead peroxide (25 grams) contained in water (100 c.c.) is gently heated, a vigorous evolution of hydrogen occurs, sodium or potassium formate being simultaneously formed, according to the equation $C_3H_8O_3 + 3O = H_2 + 3H{\cdot}COOH$. About 97 per cent. of the theoretical quantity of formic acid is produced.

Under somewhat similar circumstances ethylene glycol also yields hydrogen and formic acid (yield about 60 per cent.), $C_2H_6O_2 + 2O =$

$H_2 + 2CH_2O_2$. The authors intend to study the behaviour of lead peroxide with polyhydric alcohols in alkaline solution.

G. T. M.

Action of Ammoniacal Cupric Oxide on Carbon Compounds. By C. VINCENT and DELACHANAL (*Compt. rend.*, **109**, 615–616).—Pure sorbite is completely precipitated by ammoniacal cupric oxide, and hence cannot be separated from mannitol by means of this reagent (compare Guignet, Abstr., 1889, 1133). C. H. B.

Action of Cuprammonium Sulphate on Sorbite. By C. E. GUIGNET (*Compt. rend.*, **109**, 645).—Cuprammonium sulphate undoubtedly precipitates sorbite (preceding abstract), but it precipitates mannitol more rapidly, and by fractional precipitation the author has been able repeatedly to separate pure mannitol from liquids which also contained sorbite. C. H. B.

Sorbite. By C. VINCENT and DELACHANAL (*Compt. rend.*, **109**, 676—679).—Sorbite exists in the fruit of all the rosaceæ, and especially in pears, cherries, and plums, which contain 0·7 to 0·8 per cent.

When heated with concentrated hydriodic acid, it yields β-hexyl iodide, which boils at 167° under a pressure of 753 mm.; when heated with alcoholic potash, it yields β-hexylene, boiling at 68·5 under a pressure of 735 mm., and acetic and butyric acids when oxidised. 90 c.c. of water and 35 grams of red phosphorus were gradually mixed with 150 grams of iodine in a capacious retort, 60 grams of crystallised sorbite was added, and the mixture gently heated. An energetic reaction took place, and β-hexyl iodide was obtained in almost theoretical quantity, no resinous products being formed.

Mannitol yields the same β-hexyl iodide when treated with hydriodic acid.

When heated with acetic anhydride and a small quantity of zinc chloride, sorbite yields a hexacetate, $C_6H_8(OAc)_6$, which is obtained as a very thick, colourless syrup, on washing the crude product with water, dissolving in ether, and evaporating the filtered ethereal solutions.

It follows from these results that the constitution of anhydrous sorbite is $C_6H_8(OH)_6$. C. H. B

Transformation of Cane Sugar into Dextrose. By J. BOCK (*Chem. Centr.*, 1889, ii, 30, from *Öster-ungar. Zeit. Zucker. Ind. Landw.*, **18**, 194).—Cherries which had been preserved by heating with a hot concentrated solution of cane-sugar, and which had kept perfectly sound during the winter, were allowed to remain for four or five days in a loosely covered dish, when it was found that they were coated with a white, crystalline mass, which, after separation and recrystallisation, proved to be dextrose. Levulose was not found. The exact circumstances under which this change took place could not be determined. J. W. L.

Raffinose. By BERTHELOT (*Compt. rend.*, **109**, 548—550).—The ordinary crystals of raffinose are generally regarded as having the

composition $C_{18}H_{32}O_{16} + 5H_2O$, but raffinose from cotton seed separates from dilute alcohol in the form of a syrup, which gradually solidifies to lamellar crystals which contain 6 mols. H_2O and are different from the ordinary crystals. The rotatory power of their solution is, however, the same as that of a solution of the ordinary crystals.

The author confirms Tollens' observation, that good beer yeast ferments raffinose completely, but that weak yeast ferments only about one-third even after 48 hours, although during the same time it will completely ferment saccharose and glucose. It seems most probable that under these conditions raffinose splits up into glucose, which ferments, and either a saccharose which has a small reducing power like lactose, or a mixture of two glucoses only one of which has reducing power. C. H. B.

Fermentation of Raffinose by Beer Yeast. By D. Loiseau (*Compt. rend.*, **109**, 614—615).—In a sealed paper, dated March 5th, 1888, the author described the following results. Raffinose is completely fermented by low beer yeast, but with high beer yeast only about one-third of the total possible alcohol is formed, whilst the solution has a reducing power equivalent to that of a quantity of glucose, equivalent to the amount of raffinose which has been fermented. It is probable that 2 mols. of raffinose are converted into 1 mol. of lævogyrate glucose, which always ferments, and twice the quantity of a dextrogyrate compound which is not fermented by high yeast. Prolonged contact with acids converts this compound into glucose, which is completely fermented by both forms of yeast.

This difference in behaviour with raffinose may be used as a means of distinguishing between high aud low yeast (compare Berthelot, preceding abstract). C. H. B.

Lactose. By E. W. T. Jones (*Analyst*, **14**, 81—83).—Having obtained some very pure crystallised lactose, the author has redetermined the specific rotatory power and cupric reduction. For a solution of 5 grams of the crystals, $C_{12}H_{22}O_{11} + H_2O$, in 100 c.c., prepared hot, and of sp. gr. 1018·6 at 15·5°, the values obtained are:—

For $C_{12}H_{22}O_{11} + H_2O$.	For $C_{12}H_{22}O_{11}$.
$[\alpha]_j = 57{\cdot}5°$	60·5°
$[\alpha]_D = 51{\cdot}9$	54·6

$$CuO \times 0{\cdot}5723 = C_{12}H_{22}O_{11}.$$
$$CuO \times 0{\cdot}6024 = C_{12}H_{22}O_{11} + H_2O.$$

The determinations were made by O'Sullivan's method, the cuprous oxide being converted into cupric oxide by careful ignition and weighed.

Lactose is not affected optically, or in reducing power, by heating with citric acid, whilst cane sugar is completely inverted. The crystals do not lose their water by 24 hours' heating in a water-oven, but if dissolved iu water and re-dried, the anhydrous sugar is obtained in a few hours. M. J. S.

Methylhydrazine. By G. v. Brüning (*Annalen*, **253**, 5—14).—In order to prepare methylhydrazine, nitrosomethylcarbamide, NO·NMe·CONH$_2$, is first obtained by adding the theoretical quantity of solid sodium nitrite to a solution of methylcarbamide nitrate mixed with powdered ice. Not more than 50 grams of methylcarbamide nitrate should be used in each operation. The nitroso-compound forms small, yellow, crystalline plates, and melts at 123—124° with decomposition. It is soluble in hot water, alcohol, and ether. The aqueous solution is decomposed by prolonged boiling. *Methylhydrazine* is prepared by adding zinc-dust (4 parts) in small quantities to the nitroso-compound suspended in water (6 parts) and acetic acid ($2\frac{1}{2}$ parts); the temperature of the mixture must be kept between 5° and 15°, and the operation lasts two to three hours. The product is filtered; the filtrate acidified with hydrochloric acid, concentrated, and the thick liquid boiled with 3 parts of strong hydrochloric acid for 12 hours in a flask provided with a reflux condenser, in order to decompose the carbamide; the well-cooled liquid is then mixed with an excess of sodium hydroxide, and distilled in a current of steam, the distillation being stopped as soon as the distillate ceases to reduce Fehling's solution. The distillate consists of an aqueous solution of methylhydrazine, ammonia, and methylamine. The latter compounds are removed by boiling the solution briskly for eight hours in a flask with a reflux condenser. The methylhydrazine is converted into the acid sulphate, which is deposited on the addition of absolute alcohol to the concentrated solution. The free base is obtained by decomposing a concentrated solution of the sulphate with sodium hydroxide. The last traces of water are removed by treating the base with barium oxide in sealed tubes at 100°. Methylhydrazine, NHMe·NH$_2$, is a colourless, mobile liquid, fuming in damp air. It boils at 87° (745 mm.), and is miscible in all proportions with water, alcohol, and ether. It strongly reduces Fehling's solution at the ordinary temperature, and attacks cork, caoutchouc, and the skin. The *acid sulphate*, N_2H_3Me,H_2SO_4, forms long white needles. It melts at 139·5°, and decomposes at 182°. Unlike the normal sulphate, it is insoluble in alcohol. The *hydrochloride* is precipitated from its alcoholic solution by ether. The oxalate is soluble in warm alcohol. The picrate is deposited from alcohol in yellow, needle-shaped crystals, and melts at 162° with decomposition. *Methylsemicarbazide*, NH$_2$·CO·N$_2$H$_2$Me, prepared by the action of potassium cyanate on methylhydrazine sulphate, crystallises in prismatic plates, and melts at 113°. It is freely soluble in water and alcohol. *Methylphenylthiosemicarbazide*, NHPh·CS·N$_2$H$_2$Me, is formed by the action of phenylthiocarbimide on an aqueous solution of methylhydrazine. This compound is soluble in water and alcohol, and melts at 143°; the aqueous solution is decomposed by mineral acids. *Dibenzoylmethylhydrazine*, N_2HMeBz_2, is freely soluble in alcohol and in dilute alkalis; it melts at 143°, and crystallises in colourless needles. *Methylpicrazide*, N$_2$H$_2$Me·C$_6$H$_2$(NO$_2$)$_3$, is formed when an alcoholic solution of picryl chloride is added to a solution of the base. It crystallises in yellow plates, melts at 171° with decomposition, and is freely soluble in alcohol and ether.

Oxalyldimethylhydrazine, N$_2$H$_2$Me·C$_2$O$_2$·N$_2$H$_2$Me, melts at 221°, but

it begins to sublime about 160°. It is soluble in alcohol, and reduces Fehling's solution when gently warmed. The *nitroso*-derivative crystallises in plates, and melts at 147° with decomposition.

W. C. W.

Action of Methylhydrazine on Dialdehydes and Diketones. By K. KOHLRAUSCH (*Annalen*, **253**, 15—24).—Methylphenylhydrazine reacts with benzile at 100°, yielding *benzilemethylphenylhydrazone*, COPh·CPh:N·NMePh, a crystalline substance freely soluble in alcohol, ether, and light petroleum. It melts at 55—56°, and is completely decomposed at 200°; it is also decomposed by strong hydrochloric acid at the ordinary temperature. *Benzilemethylphenylosazone*, $C_2Ph_2(N·NMePh)_2$, is formed when a mixture of benzile (1 mol.) and methylphenylhydrazine ($2\frac{1}{2}$ mols.) is heated at 120°; the crude product is treated with hot dilute sulphuric acid to remove the excess of base, and the red, crystalline mass which is deposited when the mixture cools is purified by recrystallisation from alcohol. The pure substance forms yellow needles soluble in ether and acetone, melts at 179—180°, and is decomposed at 220°; it is not readily attacked by strong hydrochloric acid.

Glyoxalmethylphenylosazone, $C_2H_2(N·NMePh)_2$, is deposited as a yellow precipitate, when an aqueous solution of glyoxal is added to an acetic acid solution of methylphenylhydrazine. It melts at 217—218°, and is completely decomposed at 250°. This osazone does not give a characteristic coloration with ferric chloride.

Benzoylacetonemethylphenylhydrazone, $CH_2Ac·CPh:N·NMePh$, is freely soluble in ether. It melts at 103—104°, and begins to decompose at 210°. 1′.2′.3′-*Methylphenylacetylindole* is formed when methylphenylhydrazone is fused with zinc chloride. The indole melts at 136°, and dissolves freely in glacial acetic acid. It is decomposed by strong hydrochloric acid at 100°, yielding Degen's 1′.2-methylphenylindole (Abstr., 1887, 149).

Acetylacetonemethylphenylhydrazine, $CH_2Ac·CMe:N·MePh$, is a yellow oil which can be distilled in a vacuum without decomposition. The compound formed by the action of methylphenylhydrazine on an excess of acetonylacetone could not be isolated, as it undergoes spontaneous decomposition, losing a molecule of water, and changing into the methylphenylamidodimethylpyrroline described by Knorr (Abstr., 1887, 276).

Acetonylacetonemethylphenyldihydrazone, $C_2H_4(CMe:NMePh)_2$, is deposited in the form of an oil, which slowly crystallises when an aqueous solution of acetonylacetone is added to excess of methylphenylhydrazine dissolved in acetic acid. The crystals melt at 143—144°, and dissolve in alcohol, ether, benzene, and light petroleum. The dihydrazone dissolves also in hydrochloric acid; when this solution is heated, the preceding pyrroline-compound appears to be formed.

W. C. W.

Derivatives of Dichloromaleimide. By G. CIAMICIAN and P. SILBER (*Ber.*, **22**, 2490—2497).—Chloranilidomaleimide (m. p. 195—196°) is decomposed when heated above its melting point; it is soluble in ether and hot alcohol, but only sparingly in boiling water.

It dissolves in hot dilute sulphuric acid, yielding a colourless solution, and in alcoholic solutions dimethylaniline produces a reddish-brown coloration.

Chloramidomaleimide, $C_4ClO_2(NH_2)\colon NH$, is obtained in small quantity when dichloromaleimide is heated under pressure with excess of alcoholic ammonia. It crystallises from water in golden needles, melts at 220°, and is soluble in alcohol and ether, but insoluble in benzene. It dissolves in alkalis with a yellow coloration, but the solution becomes colourless on heating.

Dichloromaleamic acid, $COOH{\cdot}C_2Cl_2{\cdot}CO{\cdot}NH_2 + H_2O$, prepared by heating dichloromaleimide (8 grams) with ammonia (80 c.c.) in sealed tubes, separates from water in crystalline aggregates, melts at 175° with decomposition, and is soluble in ether, alcohol, and warm water, but insoluble in benzene. The *silver* salt, $C_4HCl_2NO_3Ag_2$, crystallises in colourless needles, and explodes when heated.

An orange-red compound, $C_{16}H_{13}N_5O_2$ or $C_{16}H_{15}N_5O_2$, separates in crystals when dichloromaleimide is heated with phenylhydrazine in alcoholic solution. This substance crystallises from boiling acetone or glacial acetic acid in orange-red needles, melts at 269—271° with decomposition, and is only sparingly soluble in most ordinary solvents. It dissolves in concentrated sulphuric acid with an intense red coloration, and on adding water an orange-red, flocculent substance is precipitated. F. S. K.

Thioaldehydes. By E. Baumann and E. Fromm (*Ber.*, **22**, 2600—2609).—β-Trithioaldehyde (Klinger, Abstr., 1879, 720) is formed when hydrogen sulphide is passed through a mixture of aldehyde (1 part) with alcohol previously saturated with hydrogen chloride (3 parts); crystals soon separate, and the whole becomes solid. The product is washed with water and crystallised from alcohol, from which it separates in long needles melting at 125—126°. A small amount of α-trithioaldehyde, melting at 101—102°, is also formed, as well as a few crystals of a substance melting at 76°, possibly Marckwald's γ-derivative (Abstr., 1886, 865).

α-Trithioaldehyde is obtained as the chief product when equal parts of aldehyde, water, and strong hydrochloric acid are used. It crystallises from acetone in splendid prisms an inch long. The β-compound is also formed.

β-Thiobenzaldehyde and γ-thiobenzaldehyde are formed when hydrogen sulphide is passed through a mixture of benzaldehyde and alcoholic hydrogen chloride. The product is boiled with benzene until almost all is dissolved; on cooling, the β-compound separates in crystals having the composition $3C_7H_6S + C_6H_6$ (not $C_7H_6S + C_6H_6$, Klinger); this gives up all the benzene at 160°, and a portion when kept at the ordinary temperature for a long time.

γ-Thiobenzaldehyde, C_7H_6S, crystallises from benzene in small, pointed needles melting at 166—167°. The crystals contain no benzene of crystallisation. When the solution in benzene is treated with iodine, the whole solidifies after some time, being converted into the β-derivative.

When α- or β-trithioaldehyde is oxidised with potassium perman-

ganate, they both give as end-product a *trisulphone*, $C_6H_{12}S_3O_6$, together with products containing less oxygen (compare Guareschi, Abstr., 1884, 294). This forms slender needles, softens at 340°, becoming yellow, and sublimes at a higher temperature without melting. It is almost insoluble in water, very sparingly soluble in alcohol, ether, chloroform, and benzene, more soluble in hot acetic acid; it also dissolves readily in strong nitric or sulphuric acid, but is precipitated by water. Alkalis dissolve it readily, and it can be crystallised from ammonia and alkaline carbonates. The constitution of trithioaldehyde sulphone is $SO_2<\begin{matrix}CHMe\cdot SO_2\\CHMe\cdot SO_2\end{matrix}>CHMe$. When an alcoholic alkaline solution of the substance is treated with methyl iodide, the compound $C_9H_{18}S_3O_6$, melting at 302°, is formed. In a similar manner, ethyl-, allyl-, and benzyl-groups may be added.

N. H. M.

Thio-derivatives of Ketones. By E. BAUMANN and E. FROMM (*Ber.*, **22**, 2592—2599; compare Abstr., 1889, 852).—*Thioacetone* $CSMe_2$, is formed as a readily volatile oil in the preparation of trithioacetone and tetrathioacetone (*loc. cit.*), but was not isolated owing to its instability and the difficulty of separating it from trithioacetone. It is also produced, together with ethyl sulphide and other sulphur-derivatives, when acetone-ethylmercaptole, $CMe_2(SEt)_2$, is heated above 160°. Owing to the very unpleasant odour of the compound, which is stronger than that of any other known substance, the smallest traces of it being sufficient to infect whole districts, the study of the compound was not continued.

Trithioacetone is decomposed by strong nitric acid with explosive violence.

A further examination of the sulphone obtained by oxidising trithioacetone with potassium permanganate (*loc. cit.*), showed that this could be separated by crystallisation from alcohol into two substances. The more sparingly soluble compound, *triacetonetrisulphone*, $C_9H_{18}S_3O_6$, crystallises from glacial acetic acid in slender needles which melt at 302° (uncorr.), and sublime readily. The more readily soluble compound, $C_9H_{18}S_3O_4$, is probably *trithioacetonedisulphone;* it melts at 208°.

Acetonetrisulphone is not changed by acids and alkalis; it dissolves in strong acids, and is precipitated by water unchanged. Boiling fuming nitric acid has no action on it. Its constitution is probably $CMe_2<\begin{matrix}SO_2\cdot CMe_2\\SO_2\cdot CMe_2\end{matrix}>SO_2$.

The compound $C_9H_{18}S_3O_4$ dissolves in bromine, yielding an unstable bromine-derivative, which readily decomposes with evolution of hydrogen bromide. When gently heated with fuming nitric acid, the compound is oxidised with formation of much sulphuric acid. Probably the substance has the constitution $S<\begin{matrix}CMe_2\cdot SO_2\\CMe_2\cdot SO_2\end{matrix}>CMe_2$.

N. H. M.

The Introduction of Acid Radicles into Ketone Molecules. By L. CLAISEN (*Bull. Soc. Chim.* [3], 1, 496—510; compare Abstr.,

1888, 666, 671, 676, and 1889, 584, 619, 850).—A *résumé* of the author's already published work on this subject, concluding with a discussion as to the theory of the reactions. T. G. N.

Substituted Acrylic and Propiolic Acids. By C. F. Mabery and A. W. Smith (*Ber.*, 22, 2659—2660).—When $\alpha\beta$-dichloracrylic acid is dissolved in carbon bisulphide, and chlorine passed through the solution whilst it is exposed to sunlight, *tetrachloropropionic acid*, $C_2HCl_4 \cdot COOH$, gradually crystallises out. It forms large, rhombic prisms, is soluble in carbon bisulphide, chloroform, and water, and melts at 76°. Its *barium salt* crystallises in prisms; its *calcium salt* in needles; its *potassium salt* in plates. Its *silver salt* is very unstable.

When $\alpha\beta$-dichloracrylic acid is heated with hydrobromic acid in closed tubes at 110—120°, *bromodichloropropionic acid* is formed. It is soluble in water and boiling carbon bisulphide, crystallises in prisms, and melts at 75—76°.

When an aqueous solution of bromopropiolic acid is mixed with hypochlorous acid and left in the dark, *chlorobromhydroxyacrylic acid*, $C_2(OH)ClBr \cdot COOH$, is formed. It is easily soluble in boiling water, is crystalline, and melts at 104—105°. Its *silver salt* is soluble in nitric acid, and is very unstable in aqueous solution. L. T. T.

Action of Phosphorus Pentachloride on Chloralide. Tetrachlorethylidene Trichlorolactate. By R. Anschütz and A. R. Haslam (*Annalen*, 253, 121—131).—The compound of the composition $C_5HCl_7O_3$, which the authors obtained by the action of phosphorus pentachloride on chloralide (Abstr., 1887, 915), proves to be the tetrachlorethylidene trichlorolactate. It boils at 276° without decomposition. Methyl and ethyl alcohol act on this compound at the ordinary temperature, yielding hydrogen chloride and the ethyl or methyl salts of trichloracetic and trichlorolactic acids. Normal propyl and isobutyl alcohols act less energetically than ethyl alcohol. *Normal propyl trichlorolactate* boils at 115—117° under 12 mm. pressure, and at 248—250° under the ordinary atmospheric pressure. Its sp. gr. at 20°, compared with water at 4°, is 1·51628. *Isobutyl trichlorolactate* boils at 111—112° under 12 mm. pressure, and at 236—238° under the normal atmospheric pressure. Its sp. gr. at 20° is 1·53216. The chloride is slowly decomposed by water, yielding trichloracetic and trichlorolactic acids. These results indicate that the constitution of the chloride is represented by the formula

$$\begin{array}{l} CCl_3 \cdot C(OH) \\ \quad | \\ \quad COO \text{—} \end{array} \!\!> CCl \cdot CCl_3.$$

W. C. W.

Derivatives of Ethyl Acetoacetate. By R. Schönbrodt (*Annalen*, 253, 168—205).—Ethyl monochloracetoacetate is formed by passing chlorine into ethyl cupracetoacetate suspended in chloroform until the green colour of the compound changes to grey. By the prolonged action of chlorine, a dichloro-substitution-product is obtained. Analogous results are produced when bromine is used instead of chlorine; the ethylic salts of mono- and di-bromacetoacetic

acid have been described by Duisberg (*Annalen*, **213**, 152 and 143). *Ethyl iodacetoacetate*, prepared by the action of iodine on ethyl cupracetoacetate, is a yellow oil, miscible with ether and alcohol. The alcoholic solution gives a blood-red coloration with ferric chloride. The compound is unstable. It decomposes at 25° in a vacuum, and its sp. gr. at 14° is 1·7053, compared with water at the same temperature. It is converted into ethyl monochloracetoacetate by the action of silver chloride, but with silver cyanide it yields hydrogen cyanide and ethyl succinosuccinate. The product of the action of silver nitrite on ethyl iodacetoacetate is a yellow oil, probably ethyl nitroacetoacetate. This substance gives an intense blood-red coloration with ferric chloride and strong sulphuric acid. It does not yield an amido-compound on reduction with tin and hydrochloric acid, nor does it form a solid compound with hydroxylamine. It combines with phenylhydrazine, yielding phenylmethylisonitrosopyrazolone [1 : 3 : 4 : 5], described by Knorr (Abstr., 1887, 602). The same compound is formed by the action of phenylhydrazine on the ethylic salt of monochlor-, brom-, or iod-acetate. The reaction may be represented as follows: $C_6H_9ClO_3 + 3NHPh\cdot NH_2 = C_{10}H_9N_3O_2 + 2NH_2Ph + NH_4Cl + C_2H_5\cdot OH$. Bender (Abstr., 1888, 53) has shown that in the ethereal solution, phenylhydrazine and ethyl monochloracetoacetate yield the ethylic salt of β-phenyl azocrotonate. The author confirms the accuracy of this observation.

Ethyl sodacetoacetate reacts with ethyl iodacetoacetate, yielding ethyl diacetosuccinate. Metallic silver eliminates the iodine from ethyl iodacetoacetate, and forms the ethyl diacetofumarate described by Just (Abstr., 1886, 141). Ethyl thiacetoacetate, first prepared by Buchka (Abstr., 1885, 1200), is formed by boiling sulphur in a solution of ethyl cupracetoacetate in benzene. In the presence of alcohol, phosphorus acts on ethyl cupracetoacetate, forming ethyl acetoacetate and triethyl phosphite. Arsenic trichloride is reduced by the copper compound, arsenic being liberated, and ethyl monochloracetoacetate formed. Ethyl cupracetoacetate is not attacked by cyanogen, but nitrogen peroxide acts on it with formation of the nitro-compound which is produced by the action of silver nitrite on ethyl iodoacetoacetate.

Attempts to displace a hydrogen-atom by copper in ethyl methacetoacetate were unsuccessful. W. C. W.

Ethyl Thiacetoacetate. By K. Buchka and C. Sprague (*Ber.*, **22**, 2541—2556; compare Buchka, Abstr., 1885, 1200; Delisle, Abstr., 1887, 915; and Schönbrodt, preceding abstract).—Ethyl thiacetoacetate is best prepared by Delisle's method; 100 grams of ethyl acetoacetate yield 60—70 grams of pure ethyl thiacetoacetate. Molecular weight determinations by Raoult's method in glacial acetic acid solution showed that the molecular formula was $C_{12}H_{18}O_6S$. It melts at about 76°, but the melting point observed depends to a considerable extent on the rapidity of heating and on other conditions. The *sodium*-derivative, $C_{12}H_{16}O_6SNa_2$, is formed when ethyl thiacetoacetate is treated with sodium in ethereal solution.

When ethyl thiacetoacetate is treated with phenylhydrazine, hydrogen sulphide is evolved, and phenylmethylpyrazoloneketo-

phenylhydrazone (phenylmethylpyrazoloneazobenzene), melting at 156°, identical with the compound obtained by Knorr (Abstr., 1887, 601) is formed, together with a yellow substance which is insoluble in all ordinary neutral solvents. The compound obtained by Schönbrodt (*loc. cit.*) by treating ethyl chloro-, bromo-, or iodo-acetoacetate with phenylhydrazine, is not phenylmethylisonitrosopyrazolone, as stated by him, but is identical with the phenylmethylpyrazoloneketophenylhydrazone referred to above.

The yellow compound which is obtained together with phenylmethylpyrazoloneketophenylhydrazone (see above) when ethyl thiacetoacetate is treated with phenylhydrazine is decomposed when heated, but without melting; it dissolves in alkalis, and is reprecipitated on adding acids. It seems to have the composition $C_{10}H_8N_2SO$; when heated with phenylhydrazine, it is converted into phenylmethylpyrazoloneketophenylhydrazone with evolution of hydrogen sulphide, small quantities of di-phenylmethylpyrazolone being also formed.

Paratolylmethylpyrazoloneketoparatolylhydrazone,

$$C_7H_7{\cdot}N_2H{:}C{<}{\begin{matrix}CO{\cdot}N(C_7H_7)\\ CMe{=\!=}N\end{matrix}}{>}$$

is formed when ethyl thiacetoacetate is treated with paratolylhydrazine; it crystallises from chlorofrom in orange needles, melting at 216—217°. When excess of the hydrazine is employed in the above reaction, a compound, free from sulphur, and probably corresponding with di-phenylmethylpyrazolone is also obtained. If only a small quantity of the hydrazine is used, a sulphur compound, which is only soluble in alkalis, is formed; this substance is converted into tolylmethylpyrazoloneketotolylhydrazone (m. p. 216—217°) when heated with paratolylhydrazine, and when heated with phenylhydrazine it yields a compound. probably tolylmethylpyrazoloneketophenylhydrazone, which crystallises in red needles, melting at 186°.

Ethyl thiacetoacetate combines with α-naphthylhydrazine, yielding similar compounds. F. S. K.

Dithioxamide (Cyanogen Disulphydrate). By J. Formánek (*Ber.*, **22**, 2655—2656). When a saturated solution of cupric sulphate is treated with ammonia until the precipitate first formed is just redissolved, potassium cyanide added in quantity just sufficient to discharge the blue colour, and then a rapid stream of hydrogen chloride passed through the solution, the latter becomes first yellow, and then red; and if it is kept well cooled, small red crystals of the formula $NH_2{\cdot}CS{\cdot}CS{\cdot}NH_2$ gradually separate out. L. T. T.

Hydroxycitraconic Acid and its Derivatives. By P. Melikoff and M. Feldmann (*Annalen*, **253**, 87—95).—In dilute solutions, hypochlorous acid unites with citraconic acid to form chlorocitramalic acid, which has been described by Morawski (this Journ., 1875, 142), and by Gottlieb (*Annalen*, **160**, 101). The acid prepared by Gottlieb's process melts at 139°. It is converted into Morawski's hydroxycitraconic acid by the addition of potassium hydroxide in alcoholic solution.

The precipitate of potassium chloride and hydroxycitraconate is washed with alcohol and ether. It is then dissolved in water, the hydroxy-acid liberated by sulphuric acid, and extracted with ether. The acid melts at 162°, as stated by Scherks (Abstr., 1885, 513). The ethyl salt, $C_3H_4O(COOEt)_2$, has the sp. gr. of 1·1376 at 0° and 1·1167 at 22°, compared with water at the same temperatures.

Hydroxycitraconic acid dissolves in strong hydrochloric acid at 0°; and ether extracts from this solution a monochlorinated hydroxy-acid, $COOH{\cdot}CH(OH){\cdot}CClMe{\cdot}COOH$, crystallising in rhombic plates, which is an isomeride of the acid formed by the union of hypochlorous acid and citraconic acid, $COOH{\cdot}CMe(OH){\cdot}CHCl{\cdot}COOH$. This acid melts at 162°, and forms unstable salts. The compound which is formed by the addition of hydrobromic acid to hydroxycitraconic acid has already been described by Scherks (*loc. cit.*). Hydroxycitraconic acid is a glycidic acid, as it is converted into amidocitramalic acid by the action of alcoholic ammonia at 100°. The amido-acid forms short prisms, which seem to belong to the monoclinic system; it reddens litmus and decomposes carbonates. 100 c.c. of water at 18° dissolve 31 grams of the acid. It is almost insoluble in hot alcohol. The calcium and barium salts are amorphous. The hydrochloride, $OH{\cdot}C_3H_4(NH_2)(COOH)_2,HCl$, forms transparent prisms, soluble in water and alcohol. It melts at 100° with decomposition.

W. C. W.

Acetonediacetic or Hydrochelidonic Acid. By J. Volhard (*Annalen*, **253**, 206—236).—The dilactone of diacetic acid is prepared by maintaining succinic acid in a state of slow ebullition for six hours. When a small quantity of the contents of the retort no longer solidifies on cooling, but remains as a greasy mass, the operation is complete. The crude product is repeatedly extracted with boiling chloroform; on cooling, succinic anhydride is deposited in crystals, and the lactone remains in solution. The chloroform is removed by distillation, the residue dissolved in water, and the lactone is again extracted from this aqueous solution by chloroform. The lactone forms transparent rhombic prisms, $a : b : c = 0{\cdot}3649 : 1 : 0{\cdot}9816$, freely soluble in chloroform, acetone, ether, alcohol, benzene, and ethyl acetate. It melts at 75° and boils between 200 and 205° under 15 mm. pressure. The lactone dissolves in alkalis and in strong hydrochloric or hydrobromic acid yielding acetonediacetic acid, $CO(CH_2{\cdot}CH_2{\cdot}COOH)_2$, which is identical with the hydrochelidonic acid of Lieben and Haitinger (*Monatsh.*, **5**, 353), and with Marckwald's propiondicarboxylic acid (Abstr., 1888, 678)

The acid forms rhombic plates soluble in hot water and in alcohol. It melts at 143° and decomposes at a higher temperature. The normal salts of the alkali metals are very soluble in water and do not crystallise well. The acid potassium, sodium, and ammonium salts are anhydrous. The barium salt crystallises with 2 and with $2\frac{1}{2}$ mols. H_2O. The manganese salt $C_7H_8MnO_5 + 2H_2O$ forms pale pink needles. The zinc and cadmium salts crystallise in six-sided plates containing 2 mols. H_2O. The silver salt $C_7H_8Ag_2O_5$ is crystalline and insoluble in

water. The dimethyl salt melts at 56° and boils with decomposition at 276—277° (uncorr.). The sp. gr. of the diethyl salt is 1·0862 at 13°. Acetic chloride, acetic anhydride, and phosphoric anhydride convert the acid into the lactone. The phenylhydrazide of acetonediacetic acid melts at 107—108°. The phenylhydrazide of the dimethyl salt melts at 88—90° and dissolves in ether, benzene, and hot alcohol. The corresponding diethyl compound melts at 67°. The oxime of the acid crystallises in prisms and melts with decomposition at 129°. The oximes of the dimethyl and diethyl salts form needles and melt at 52° and 38° respectively. W. C. W.

Alkyl-derivatives of Methyluracil and Nitrouracil. By R. BEHREND (*Annalen*, **253**, 65—68).—Ethyl bromide does not react with free methyluracil, but it acts on potassium methyluracil forming monomethyluracil and dimethyluracil. It is probable that monethylmethyluracil is first formed. A portion of the monethylmethyluracil reacts with potassium methyluracil forming potassium monethylmethyluracil. This is attacked by ethyl bromide, yielding diethylmethyluracil. In a previous communication, the author stated that methyl iodide acts on potassium methyluracil, yielding trimethyluracil, and the dihydride of methyluracil; he now finds that the supposed dihydride is identical with the dimethyluracil described by Hoffmann (next Abstract). W. C. W.

Alkyl-derivatives of Methyluracil. By J. HOFFMANN (*Annalen*, **253**, 68—77).—Ethyl methyluracil and diethylmethyluracil are formed by the action of ethyl bromide or iodide (3 mols.) on potassium methyluracil (1 mol.) in sealed tubes at 150; the excess of ethyl bromide or iodide is removed from the crude product by distillation, the residue is dissolved in water, and the aqueous solution treated with chloroform. The chloroform extract is then dried and distilled, and the residue dissolved in boiling alcohol; on cooling, crystals of ethylmethyluracil are deposited. The mother-liquor contains monethyl- and diethyl-methyluracil. The former is deposited as a crystalline crust, but the diethyl-derivative can only be isolated by dropping a crystal of diethylmethyluracil into the mother-liquor, when crystallisation takes place. *Ethylmethyluracil* is deposited from ethyl bromide in prisms and from alcohol in needles. It is freely soluble in chloroform and in ethyl bromide, and is much more soluble in hot than in cold alcohol. A crystalline silver salt, $C_5H_4EtAgN_2O_2$, is obtained when silver nitrate is added, in sufficient quantity to produce a permanent turbidity, to a solution of ethylmethyluracil in a 10 per cent. solution of potassium hydroxide. *Diethylmethyluracil* crystallises in rhombic plates and melts at 52—53°, dissolves freely in chloroform, alcohol, ether and water, and is decomposed by potassium hydroxide at the ordinary temperature with liberation of ethylamine. Methyl bromide acts on potassium methyluracil at 140°, forming dimethyluracil and trimethyluracil. *Trimethyluracil* melts at 109°, crystallises in rhombic plates, and is freely soluble in chloroform, alcohol, and water, and sparingly soluble in ether. *Dimethyluracil* is insoluble in ether, but can

be recrystallised from hot alcohol. *Methyluracil di-iodide*, $C_5H_6N_2O_2I_2$, is formed by the action of iodine dissolved in strong hydriodic acid on methyluracil. It is an unstable compound, dissolving with decomposition in water, alcohol, and chloroform. The di-iodide forms deep violet crystals.

W. C. W.

Nitrouracil-derivatives. By M. LEHMANN (*Annalen*, **253**, 77—87).—*Methylnitrouracil*, $C_5H_5N_3O_4 + H_2O$, is formed by the action of methyl iodide on potassium nitrouracil in sealed tubes at 140°. It crystallises in long needles and is solnble in hot water. 100 c.c. of water at 20° dissolve 0·714 gram, and 100 c.c. of alcohol at 17° dissolve 0·115 gram of the substance. It is less soluble in ether, chloroform, benzene, and methyl iodide than in water. The potassium, silver and barium salts are crystalline; the silver and barium salts are almost insoluble in cold water. *Methylisobarbituric acid*, $C_5H_6N_2O_3$, is deposited in crystals when methylnitrouracil is reduced by tin and hydrochloric acid; the mother-liquor contains methylamidouracil in small quantity. A neutral solution of methylamidouracil hydrochloride turns red on the addition of potassium cyanate; the colour is destroyed by hydrochloric acid, and *methylhydroxyxanthine*, $C_6H_8N_4O_3$. is deposited as a yellow, crystalline powder. 100 c.c. of water at 16° dissolve 0·16 gram of methylhydroxyxanthine. Methylnitrouracil is decomposed by baryta-water at 160—170°, with liberation of methylamine; dimethylnitrouracil under similar treatment yields dimethylamine. Dimethylnitrouracil melts at 154·5° and is deposited from hot water in needles containing 1 mol. H_2O. It does not unite with bases to form salts. The constitution of methyl- and dimethyl-nitrouracil can be represented by the formulæ, $CO<\genfrac{}{}{0pt}{}{NH\cdot CH}{NMe\cdot CO}>C\cdot NO_2$ and $CO<\genfrac{}{}{0pt}{}{NH\cdot CMe}{NMe\cdot CO}>C\cdot NO_2$. Methylnitromethyluracil, prepared by the action of methyl iodide on potassium nitromethyluracil, crystallises in needles and melts at 149°. It unites with bases, forming crystalline salts. *Ethylnitrouracil*, $C_6H_7N_3O_4 + H_2O$, forms silky needles and melts at 194·5; it is deposited from alcohol in anhydrous crystals, and is soluble in hot water, ether, chloroform, benzene, and ethyl bromide. The potassium and silver salts crystallise in needles.

Ethylisobarbituric acid, $C_6H_8N_2O_3$, melts at 250°, but begins to decompose at 230°. It is soluble in hot, but almost insoluble in cold water. *Ethylhdroxyxanthine* crystallises in prisms which turn pink on exposure to the air. *Ethylmethylnitrouracil*, $CO<\genfrac{}{}{0pt}{}{NEt\cdot CH}{NMe\cdot CO}>C\cdot NO_2$, crystallises from hot water in needles, containing 1 mol. H_2O. The crystals effloresce; it melts at 109°. *Methylethylnitrouracil*, $CO<\genfrac{}{}{0pt}{}{NMe\cdot CH}{NEt\cdot CO}>C\cdot NO_2$, melts at 73° and crystallises in rhombohedra, containing 1 mol. H_2O. The substance becomes anhydrous at 90°, and remains liquid at the ordinary temperature, but solidifies on the addition of water. It is freely soluble in alcohol and ether.

W. C. W.

Fucusol. By MAQUENNE (*Compt. rend.*, **109**, 571--573).—Dried *Fucus vesiculosus* was heated in an oil-bath at 160° with 4·5 parts of sulphuric acid of 20° B and the product, after neutralisation, was distilled and fractionated. Small quantities of water and acetone were obtained, together with two fractions boiling at 162—163° and 185—187° respectively. The fraction 162—163° consists of pure furfuraldehyde : the fraction 185—187° is *methylfurfuraldehyde*, a liquid of sp. gr. 1·105 at 15°. With ammonia, it yields a crystalline product closely resembling furfuramide; its hydrazone is an oily liquid; with silver oxide, it yields methylpyromucic acid, melting at 108—109°. When treated with hydriodic acid, it resinifies but does not carbonise, and does not become green; the product yields iodoform when mixed with potassium hydroxide. With acetic anhydride in presence of fused sodium acetate, it yields methylfurfuracrylic acid melting at 157° and crystallising from boiling water or alcohol in small, white needles which retain about $\frac{1}{3}$ mol. H_2O. If methylfurfuraldehyde is heated with strong hydrochloric acid, it becomes green, a reaction which Stenhouse observed with fucusol. The following reaction serves to detect methylfurfuraldehyde in presence of a large proportion of furfuraldehyde. One drop of the liquid is dissolved in 5—6 c.c. of alcohol of 90° and 1 c.c. of sulphuric acid of 60° is added slowly without agitation; a green coloration appears at the junction of the two liquids. The coloration persists even after agitation if the methylfurfuraldehyde is abundant, but changes to grey if furfuraldehyde is in excess. The reaction is similar to that given by heptine (or its oxidation-products) from perseitol.

This methylfurfuraldehyde is identical with that obtained by Hill from wood tar.

Fucusol is not a distinct compound, as Stenhouse supposed, but is a mixture of furfuraldehyde with about 10 per cent. of methylfurfuraldehyde. C. H. B.

Relation between Sugars and Furfuran-derivatives. By MAQUENNE (*Compt. rend.*, **109**, 603—606).—Methylfurfuraldehyde from *Fucus* (preceding Abstr.) yields acetic acid on oxidation, and hence contains a terminal methyl-group, and is one of the three isomerides which contain the methyl-group in the position 2, 3, or 4 with respect to the aldehyde group. It has the same relation to isodulcitol or rhamnose, $C_6H_{12}O_5$, as furfuraldehyde has to arabinose, $C_5H_{10}O_5$.

Crystallised isodulcitol distilled with four times its weight of sulphuric acid of 15 to 20° B yields a small quantity of acetone, together with pure methylfurfuraldehyde identical with that from *Fucus vesiculosus* or wood tar, but no furfuraldehyde is obtained. Fischer and Tafel have shown that isodulcitol is an aldehyde derived from normal hexane, and according to Herzig it yields acetic acid on oxidation, and hence contains a terminal methyl-group. Its conversion into methylfurfuraldehyde would involve the union of the chains 2 and 5 by means of an atom of oxygen, the methyl-group occupying the position 4, thus:—

$$O{<}\begin{matrix}CMe{:}CH\\C(CHO)\end{matrix}{\gg}CH.$$

Since furfuraldehyde is obtained from arabinose by dehydration, it follows that isodulcitol is ω-methylarabinose, a relation which has often been suggested, but has never previously been established.

The yield of methylfurfuraldehyde from isodulcitol is small, but it suffices to detect the isodulcitol in substances in which its presence is not recognised by the usual methods, and it has been detected in several plants in which it was not known to exist. Since *Fucus vesiculosus* yields methylfurfuraldehyde (*loc. cit.*), it would seem that isodulcitol exists in marine plants. C. H. B.

Selenium and Oxygen-derivatives in the Benzene Series. By C. CHABRIÉ (*Compt. rend.*, **109**, 568—570).—The action of nitric acid on phenyl selenide (Abstr., 1889, 1167), yields nitro-derivatives; potassium permanganate or chromic acid yields indefinite oxidation-products; hydrogen peroxide and hydrochloric acid yield compounds in which oxygen has been introduced into the phenyl-group.

The action of selenious chloride, $SeOCl_2$, on benzene in presence of aluminium chloride yields two compounds according to the proportions of the reacting bodies. *Diphenylselenone*, $SeOPh_2$, is an amber-yellow liquid which boils at 230° under a pressure of 65 mm.; sp. gr. at 19·6 = 1·48. The other product, $PhSeO·C_6H_4Cl$, crystallises in white, hexagonal, prismatic lamellæ with a fatty lustre; it melts at 94°, boils at 230° under a pressure of a few millimetres, is insoluble in water, but dissolves in alcohol, and is attacked by cold nitric acid.

Diphenylselenine when treated with bromine water yields the compound, $SeO(C_6H_4Br)_2$, which crystallises from alcohol in modified rhombic prisms melting at 120°. When mixed with hydrogen peroxide and hydrochloric acid and treated with a current of air, diphenylselenine yields the compound, $SeO(C_6H_4Cl)_2$ or $PhSeO·C_6H_3Cl_2$, which crystallises from boiling alcohol in small, white prisms, melts at 159°, and is not attacked by cold nitric acid.

The action of the compound $Se(OH)_2Cl_2$ on benzene in presence of aluminium chloride yields diphenylselenine and selenophenol.

C. H. B.

Action of Phosphorus Trichloride on Phenol. By R. ANSCHÜTZ and W. O. EMERY (*Amer. Chem. J.*, **11**, 379—387).—By the action of phosphorus trichloride on phenol, the following three compounds were formed (compare Noack, Abstr., 1883, 735), and were separated by distillation under greatly diminished pressure:—

Phenylphosphoryl dichloride, $PCl_2·OPh$; sp. gr. 1·3542 at 20° (water at 4° = 1); boiling at 90° under 11 mm. pressure; *diphenylphosphoryl chloride*, $PCl(OPh)_2$; sp. gr. 1·24378 at 20° (water at 4° = 1); boiling at 172° under 11 mm. pressure; *triphenyl phosphite*, $P(OPh)_3$; sp. gr. 1·18428 at 20° (water at 4° = 1); boiling at 220° under 11 mm. pressure.

The action of phosphorus pentachloride on the preceding compounds was investigated. In the cold, no action takes place; at 100° crystalline compounds are formed, soluble in chloroform and carbon tetrachloride. Chlorine additive-products were almost certainly formed, but they could not be isolated; they were, however,

obtained by passing dry chlorine over solutions of the phosphorous compounds in dry ether. *Phenylphosphoryl tetrachloride*, $PCl_4\cdot OPh$, prepared from chlorine and phenylphosphoryl dichloride, forms small plates, soluble in chloroform and carbon tetrachloride, insoluble in ether; it is deliquescent, and is decomposed by water, normal phenyl phosphate being formed. With sulphurous anhydride, it behaves like the corresponding phosphenyl compound, giving thionyl chloride and the oxychloride, $POCl_2\cdot OPh$, boiling at 121—122° under 11 mm. pressure. *Diphenylphosphoryl trichloride*, $PCl_3(OPh)_2$, formed from chlorine and diphenylphosphoryl chloride, is a yellow oil, solidifying to minute crystals, soluble in chloroform, insoluble in ether; it easily decomposes when heated, and also when treated with water, in which case phenyl phosphate is formed. *Triphenylphosphoryl dichloride*, $PCl_2(OPh)_3$, prepared from chlorine and phenyl phosphite, solidifies at a very low temperature; when treated with water, it decomposes into phenyl phosphate and hydrochloric acid.

By the addition of dry bromine to ethereal solutions of the mono- and di-chlorides, the compounds $PCl_2Br_2\cdot OPh$ and $PClBr_2(OPh)_2$ were obtained; these are very unstable substances.

Phenylphosphoryl thiochloride, $PSCl_2\cdot OPh$, was obtained by heating phenylphosphoryl dichloride with sulphur at 190°; it has a sp. gr. of 1·40593 at 20° (water at 4° = 1), boils at 119—120° under 11 mm. pressure, and is a highly refractive liquid, soluble in ether and chloroform. *Diphenylphosphoryl thiochloride*, $PSCl(OPh)_2$, prepared from diphenylphosphoryl chloride and sulphur heated at 190°; melts at 63—64°, and boils at 194° under 11 mm. pressure. Attempts to obtain the preceding two compounds by heating together phenol and phosphorus thiochloride were unsuccessful, hydrogen chloride and normal phenyl phosphate being formed. *Triphenyl thiophosphate*, $PS(OPh)_3$, was obtained by heating phenyl phosphite with sulphur at 190°; it forms crystalline needles melting at 49—50°, and boiling at 245° under 11 mm. pressure; sp. gr. = 1·24411 at 20° (water at 4° = 1). It is found that these thio-compounds have very nearly the same melting points and boiling points as the corresponding oxy-compounds.

The existence of the compound $PCl_4\cdot OPh$ leads to the following view of the action of phosphorus pentachloride on hydroxy-compounds:—

$$R\cdot OH + PCl_5 = HCl + RO\cdot PCl_4 \text{ and } RO\cdot PCl_4 = POCl_3 + RCl.$$

C. F. B.

Apiole. By G. Ciamician and P. Silber (*Ber.*, **22**, 2481—2490; compare Abstr., 1888, 1100).—The authors give the name *apionole* to the tetrahydroxybenzene which forms the basis of apiole; the dimethyl ether of tetrahydroxybenzene is, therefore, dimethylapionole, and "apione" is dimethylmethyleneapionole.

Dimethylapionole, $C_6H_2(OH)_2(OMe)_2$, is obtained when apiolic acid (2·5 grams) is heated at 180° for 4 to 6 hours with potash (8 grams) and alcohol (10 c.c.). It melts at 105—106° and boils at 298°. In aqueous solutions, ferrous sulphate produces, after some time, a blue coloration, lead acetate a gelatinous precipitate, and silver nitrate a

crystalline precipitate, which immediately turns black. It dissolves in concentrated sulphuric acid, yielding a yellow solution, which quickly turns red, and on warming becomes violet. The *diacetyl-derivative*, $C_6H_2(OMe)_2(OAc)_2$, crystallises from alcohol, melts at 144°, and is soluble in ether, warm alcohol, and glacial acetic acid, but only sparingly in hot, and insoluble in cold water. It dissolves in warm, concentrated sulphuric acid, yielding a colourless solution, which turns yellow and then brown on heating more strongly.

Tetramethylapionole, $C_6H_2(OMe)_4$, prepared by treating the dimethyl-derivative with methyl iodide in methyl alcoholic potash solution, crystallises from hot water in colourless needles, melts at 81°, and is readily soluble in alcohol, ether, benzene, acetone, and acetic acid, but only sparingly in water. It dissolves in concentrated sulphuric acid, yielding a colourless solution, which turns brownish-red on warming, and in concentrated nitric acid with a yellow coloration. It is not acted on by hydrochloric acid at 100°, but at higher temperatures it is decomposed with evolution of methyl chloride.

Apioneacrylic acid, $CH_2{:}O_2{:}C_6H(OMe)_2{\cdot}CH{:}CH{\cdot}COOH$, prepared by boiling apiolaldehyde with acetic anhydride and sodium acetate, crystallises from hot alcohol in small, yellow needles, melts at 196°, and is readily soluble in hot glacial acetic acid, benzene, and alcohol, but only sparingly in ether and hot water, and almost insoluble in cold water. It dissolves in concentrated sulphuric acid with a yellow coloration, the solution turning brown on warming. The *sodium* salt crystallises in microscopic needles, and is readily soluble in water; in an aqueous solution of the sodium salt, lead acetate, barium chloride, calcium chloride, or zinc sulphate produces a colourless, nickel nitrate or copper sulphate a green, cobalt nitrate a red, silver nitrate a light yellow, and ferric chloride a reddish-brown precipitate.

Apionecrotonic acid, $CH_2{:}O_2{:}C_6H(OMe)_2{\cdot}CH{:}CMe{\cdot}COOH$, prepared from apiolaldehyde in like manner, crystallises from alcohol in light yellow needles, melts at 209°, and is almost insoluble in water, but soluble in ether, hot alcohol, and hot acetic acid. It dissolves in concentrated sulphuric acid with a yellow coloration, the solution turning bluish-green on warming. The *sodium* salt is readily soluble in water. The *calcium* salt, $(C_{13}H_{13}O_6)_2Ca + 5H_2O$, crystallises from hot water in broad, colourless needles, and loses its water at 100°. The *silver* salt, $C_{13}H_{13}O_6Ag$, is colourless, and very sparingly soluble in water. In aqueous solutions of the sodium salt, barium chloride, magnesium sulphate, or zinc sulphate produces a white crystalline precipitate, and solutions of copper, nickel, cobalt, and ferric salts also give a precipitation. When the calcium salt is distilled with lime, a small quantity of a crystalline compound, melting at 83°, is obtained.

When calcium apiolate is distilled with lime, it yields a mixture of substances, some of which are volatile with steam; the non-volatile residue crystallises from alcohol in needles, melts at 71—72°, and seems to have the composition $C_9H_8O_5$.

The nitro-compound (m. p. 117—118°) previously described (*loc. cit.*), and obtained by treating apiolic acid with nitric acid of sp. gr. 1·4 in glacial acetic acid solution, has the composition $C_9H_8N_2O_8$, not $C_9H_6N_2O_7$, as previously given, and is probably dinitrapione.

The nitro-compound (m. p. 116°), prepared from isapiole by Ginsberg (Abstr., 1888, 722), is probably identical with dinitrapione, and the compound (m. p. 137—138°) obtained by the authors from apiolaldehyde is probably a nitro-derivative of apiolaldehyde.

F. S. K.

Chlorination and Bromination of Aniline, Orthotoluidine, and Paratoluidine in presence of Excess of a Mineral Acid. By R. Hafner (*Ber.*, 22, 2524—2541).—When chlorine is passed into an ice-cold solution of aniline in excess of 97 per cent. sulphuric acid for about 18 hours, almost the whole of the aniline remains unchanged, only small quantities of parachloraniline being formed. Under the same conditions, but employing 65 per cent. sulphuric acid, symmetrical trichloraniline (m. p. 77°), traces of a compound melting at 63—64°, probably trichlorophenol (m. p. 67—68°), and considerable quantities of resinous products are formed, but a large quantity of aniline remains unchanged. Chlorine acts energetically on aniline in 40 per cent. ice-cold sulphuric acid solution; the principal product is trichloraniline, but trichlorophenol, resinous products, and traces of other compounds, probably chloraniline and dichloraniline, are also formed.

When chlorine is passed into an ice-cold solution of aniline in excess of very concentrated (40 per cent.) hydrochloric acid for about 18 hours, most of the base is converted into parachloraniline and trichloraniline, but considerable quantities remain unchanged. Trichloraniline is also formed when chlorine ($\frac{1}{2}$ mol.) is passed into a solution of aniline (1 mol.) in ice-cold, concentrated hydrochloric acid. In 30 per cent. ice-cold hydrochloric acid solution, chlorine acts on aniline much more readily; parachloraniline, dichloraniline, symmetrical trichloraniline, and other compounds, probably chloroderivatives of phenol, are formed, and none of the base remains unchanged. In 20 per cent. hydrochloric acid solution under the same conditions, trichloraniline, chlorophenols, and large quantities of resinous products are formed.

Bromine, even when added in large excess, has no appreciable action on aniline in 97 per cent. sulphuric acid solution; after four months' time, only small quantities of symmetrical tribromaniline are formed. If a small quantity of iodine is mixed with the bromine, the formation of tribromaniline takes place rather more readily. In 65 per cent. and in 40 per cent. ice-cold sulphuric acid solution, aniline is acted on by excess of bromine, considerable quantities of tribromaniline being formed; in the latter case small quantities of a compound, probably tribromophenol, are also formed. When aniline is treated with excess of bromine in 40 per cent. hydrochloric acid solution, a reaction immediately takes place, and the whole of the base is converted into tribromaniline; in 20 per cent. hydrochloric acid solution, small quantities of tribromophenol are also formed.

Aniline hydrobromide is completely converted into tribromaniline when treated with excess of bromine in a concentrated ice-cold solution of potassium bromide; the yield of the pure product is 90 per cent. of the theoretical quantity.

When chlorine is passed into an ice-cold 97 per cent. sulphuric acid

solution of paratoluidine for about 24 hours, metachloroparatoluidine [Me : Cl : NH_2 = 1 : 3 : 4] and larger quantities of orthochloroparatoluidine [Me : Cl : NH_2 = 1 : 2 : 4] are obtained, but a considerable quantity of the base remains unchanged. In 40 per cent. hydrochloric acid solution, the whole of the paratoluidine enters into reaction, yielding metachloroparatoluidine, metadichloroparatoluidine [Me : Cl_2 : NH_2 = 1 : 3 : 5 : 4], a crystalline compound, probably orthochloroparatoluidine, and oily products, probably chlorinated derivatives of cresol.

When paratoluidine is treated with excess of bromine in 39 per cent. ice-cold hydrochloric acid solution, it is almost completely converted into metadibromoparatoluidine, melting at 73—74°, very small quantities of a bromocresol being also produced. In 65 per cent. sulphuric acid solution under the same conditions, large quantities of metadibromoparatoluidine are formed.

When orthotoluidine is treated with excess of chlorine in 98 per cent. ice-cold sulphuric acid solution, it is partially converted into a chlorotoluidine; bromine under the same conditions has no appreciable action, even after eight days' time. F. S. K.

Action of Nascent Nitrous Acid on various Amines and Phenols. By A. Deninger (*J. pr. Chem.* [2], **40**, 296—302).—When sodium nitrite (3 mols.) acts on an aqueous acid solution of aniline, ortho- and para-nitrophenol and some resinous substances are produced, in quantities dependent on the concentration, acidity, and temperature. The quantity of orthonitrophenol produced is greater, the more rapid the reaction, and the higher the temperatnre above 65°; it varies from 0 to 50 grams, whilst that of paranitrophenol varies from 0 to 33 grams per 100 grams of aniline. Air blown through the liquid diminishes the quantity of phenols produced, as also does the presence of oxidising or reducing substances. The nature of the acid has no apparent effect. To obtain the best yield, 10 grams of aniline, 20 c.c. of sulphuric acid, and 80 c.c. of water are mixed and cooled to 15°; 300 grams of sodium nitrite in 100 c.c. of water are then added, the solution heated in a water-bath and a large quantity of hot dilute sulphuric acid (1 : 1) immediately added. After the reaction, the ortho-compound is distilled over with steam, and the para-compound crystallised from the residue. Nitric oxide alone appears to be evolved during the reaction.

If orthotoluidine (10 grams) be substitned for aniline in the above process, orthonitrocresol [Me : OH : NO_2 = 1 : 2 : 3] (5 to 6 grams), melting at 68—69°, is obtained. By using a more dilute solution and allowing it to stand for 14 days at 15—20° paranitrocresol [Me : OH : NO_2 = 1 : 2 : 5], melting at 96° is obtained. With paratoluidine (100 grams) only one nitrocresol (138 grams), melting at 33—34°, is obtainable.

By acting on diamidoparadiphenyl and diamidoparaditolyl respectively with sodium nitrite (6 mols.) in the way described above, dinitrodiphenol (m. p. 260°) and dinitrodicresol (m. p. 270°) are produced respectively.

The *sulphate* of diamidodicresol (Abstr., 1888, 838), obtained by

reducing the dinitrocresol, is sparingly soluble in water; by diazotising it and decomposing with hot sulphuric acid, *tetrahydroxyditolyl* is obtained as a pleasant-smelling oil, which is volatile with steam; its aqueous solution gives a yellowish-white precipitate with ferric chloride.

With naphthylamine, the above treatment yields dinitronaphthol and a little nitronaphthol; when α-naphthylamine is treated with 2 mols. more sodium nitrite than is necessary for diazotising, and distilled at once with steam, β-nitro-α-naphthol (m.p. 128°) is obtained; but if allowed to stand for 14 days at 10—15° α-nitro-α-naphthol is formed. β-naphthylamine yields α-nitro-β-naphthol (m. p. 103°).

Sulphanilic and orthotoluidinesulphonic acids yield by this treatment garnet-red crystals, which lose the sulphonic acid group when treated with super-heated steam and yield nitrophenol and nitrocresol respectively. Naphthionic acid yields nitronaphtholsulphonic acid.

Salicylic acid and its ethereal salts yield nitrosalicylic acid and its ethereal salts.

A new substance is obtained when paraphenolsulphonic acid is treated with sodium nitrite and sulphuric acid; it is still under investigation. A. G. B.

Some Nitrated Diazoamido-compounds. By S. NIEMENTOWSKI (*Ber.*, **22**, 2562—2567).—When metanitraniline is diazotised in the manner described by Sandmeyer for paranitraniline (Abstr., 1885, 981) a resinous precipitate is formed the moment the sodium nitrite solution is added. This can be afterwards separated from the metanitrobenzonitrile by steam distillation. It crystallises from amyl alcohol in lustrous, golden needles, which melt at 191—192° with decomposition. It has the formula $C_{12}H_9N_5O_4$, and is identical with Griess' metadiazoamidonitrobenzene (m. p. 195·5, *Annalen*, **121**, 272) and with Hallmann's dinitroamidoazobenzene (m. p. 175—176°, *Ber.*, **9**, 389). In order to determine the constitution of the compound, a quantity of it was prepared by Hallmann's method; the substance prepared by this method when crystallised from amyl alcohol also gave the m. p. 195°. When the compound is heated with hydrochloric acid (sp. gr. = 1·17) for 10 hours at 185°, metachloronitrobenzene is formed. Amyl alcohol decomposes it at 185° with formation of metanitraniline and nitrobenzene. These reactions and the behaviour of the substance towards aromatic amines and phenols, with which it yields dyes, show that the compound is diazoamidonitrobenzene. Hallmann's method (*loc. cit.*) is a very convenient one for the preparation of nitrated diazoamido-compounds.

Diazoamidonitrotoluene, $C_{14}H_{13}N_3O_4$ (from metanitroparatoluidine), is prepared by treating metanitroparatoluidine (m. p. 114°, 30·4 grams), suspended in alcohol (250 grams) with nitric acid (sp. gr. 1·52, 7·5 grams), and with a saturated solution of potassium nitrite (8·5 grams). It crystallises from amyl alcohol in dark reddish-brown branched needles, melts at 163°, dissolves very sparingly in alcohol,

more readily in ether and carbon bisulphide, and very easily in cold benzene, acetone, and chloroform. When heated with alcohol at 170°, it is decomposed into metanitroparatoluidine and metanitrotoluene.

Diazoamidonitrotoluene (from paranitro-orthotoluidine, m. p. 107°) crystallises from alcohol in long, bright yellow needles, melts at 212° with decomposition, and is readily soluble in acetone, benzene, and chloroform. N. H. M.

Trinitrohydrazobenzene. By E. FISCHER (*Annalen*, **253**, 1—5). —The author's process for preparing trinitrohydrazobenzene from picryl chloride and phenylhydrazine has been criticised by Willgerodt and Ferko (Abstr., 1888, 830). In reply, the author maintains that the process yields good results, if the necessary conditions are observed. W. C. W.

Symmetrical Nitrophenylhydrazines of the Aromatic Series. By C. WILLGERODT (*J. pr. Chem.* [2], **40**, 264—270).—Symmetrical picrylhydrazines are obtained by cohabating picryl chloride and the hydrochloride of the aromatic hydrazine (in molecular proportion) in alcohol at the ordinary temperature. Picrylphenylhydrazine, *picrylorthotolylhydrazine*, *picrylparatolyhydrazine*, and *picryl-α-naphthylhydrazine* have been thus obtained.

All these decompose before they melt, at temperatures dependent on their state of division; thus picrylphenylhydrazine in powder decomposes at 177°, whereas its crystals decompose at 181° (compare Abstr., 1888, 829).

The author has studied the action of heat on the nitrophenylhydrazines in presence of various liquids and finds that the decompositions which occur may be classified as follows:—(1.) The liquid does not decompose the nitrohydrazine *per se*; in this case the hydrazine hydrogen reduces the nitro-group to a nitroso-group; such liquids are water, dilute hydrochloric acid, benzene, and glacial acetic acid. (2.) The liquid is an oxidising agent; the nitrohydrazine is oxidised to a nitroazo-compound. (3.) The liquid decomposes the nitrohydrazine altogether. (4.) The liquid acts as a reducing agent, such liquids being ethyl and methyl alcohols, formic acid, and acetone; the first two and acetone convert picrylhydrazine into dinitrosonitroazobenzene, melting at 219—220°; formic acid converts it into a mixture of two substances, melting at 225° and 233°. (5.) The liquid is an organic base; in this case the nitrohydrazine is first converted into nitro-nitroso-azo-compounds, and these into polyazo-compounds.

The paper concludes with a reply to Freund (Abstr., 1889, 977) who criticises the author's and Ferko's former work (Abstr., 1888, 829). A. G. B.

Phenylhydrazone. By E. FISCHER and F. ACH (*Annalen*, **253**, 57—65).—*Acetonedinitrophenylhydrazone*, $C_9H_{10}N_4O_4$, is prepared by slowly adding acetonephenylhydrazone (12 grams) to strong, colourless nitric acid (25 grams) surrounded by a freezing mixture; this solution is allowed to drop into 100 grams of well-cooled fuming nitric acid and the mixture is poured into ice water; the product is

extracted with small quantities of ether and the residue purified by recrystallisation from alcohol. It melts at 127° (uncorr.), is soluble in benzene, chloroform, ether, and in hot alcohol, and is quickly decomposed by hot alkaline solutions, but less readily by acids. Phenylhydrazonelevulinic anhydride is converted into the paranitro-derivative, $NO_2{\cdot}C_6H_4{\cdot}N{<}{}^{N:CMe}_{CO{\cdot}CH_2}{>}CH_2$, by fuming nitric acid. This substance crystallises in flat needles of a yellow colour, is soluble in hot alcohol, benzene, and glacial acetic acid, and melts at 118—119°. The alcoholic solution is converted into paraphenylenediamine by reduction with zinc-dust and acetic acid. Warm alcoholic potassium hydroxide or warm concentrated hydrochloric acid converts the anhydride into paranitrophenylhydrazonelevulinic acid, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}CMe{\cdot}C_2H_4{\cdot}COOH$. This acid forms orange-coloured needles soluble in acetone and hot alcohol; it also dissolves in alkalis, forming intense deep-red solutions. It darkens at 190° and melts with decomposition at 200°. The *ethyl* salt melts at 156—157° with slight decomposition. It crystallises in needles and dissolves freely in hot alcohol, benzene, and glacial acetic acid.

The hydrazones of acetone and of acetaldehyde, propaldehyde, and œnanthaldehyde are decomposed by gently warming with pyruvic acid; acetone or aldehyde is liberated and phenylhydrazonepyruvic acid is produced. The ketones and γ-ketonic acids behave in the same way.

Paranitrophenylhydrazonepyruvic acid, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}CMe{\cdot}COOH$, is precipitated when pyruvic acid is added to a hot dilute solution of nitrophenylhydrazonelevulinic acid in hydrochloric acid. The acid is soluble in acetone and in warm alcohol, and is decomposed by heat.

W. C. W.

Amidoximes and Azoximes. By F. Tiemann (*Ber.*, **22**, 2391—2395; compare Abst., 1886, 875).—The conversion of nitriles into amidoximes by the action of hydroxylamine may be considered to be a general reaction, as hitherto it has been found to apply to all cases, except that of nitriles such as pentamethylbenzonitrile, which cannot be, or are only with difficulty, converted into the corresponding acid by the usual reagents. As a rule, the formation of the amidoxime takes place much more slowly with nitriles of high molecular weight and rich in carbon, and the acid character of the product is less marked.

The amidoximes combine readily with hydrogen cyanate, phenylcarbimide, and phenylthiocarbimide, yielding uramidoximes, phenyluramidoximes, and phenylthiuramidoximes. The ethyl-derivatives of the amidoximes also combine with phenylthiocarbimide and with phenylcarbimide.

F. S. K.

Phenylallenylamidoxime-derivatives. By H. Wolff (*Ber.*, **22**, 2395—2401; compare Abstr., 1886, 798).—*Phenylallenylethoxime nitrite*, $CHPh{:}CH{\cdot}C(N{\cdot}OEt){\cdot}O{\cdot}NO$, separates in colourless needles when a solution of phenylallenylamidethoxime (1 mol.) in dilute sulphuric acid is treated with sodium nitrite (2 mols.) in the cold.

It turns yellow after a short time and is very unstable, exploding slightly when treated with concentrated sulphuric acid, or when heated quickly. It melts at 61°, is readily soluble in alcohol, chloroform, benzene, and ether, but only sparingly in light petroleum, and almost insoluble in water. It can be crystallised from alcohol at temperatures below 55°, but slight decomposition occurs. It is decomposed by acids or alkalis, yielding cinnamic acid. The *chloride*, CHPh:CH·CCl:N·OEt, separates as a yellowish oil when the amidethoxime is dissolved in excess of hydrochloric acid, and the solution treated with sodium nitrite. It is soluble in ether, alcohol, benzene, and chloroform, but only sparingly soluble in light petroleum and carbon bisulphide, and almost insoluble in water; it is not decomposed when warmed for a short time with acids or bases.

Phenyldibromopropenylethoxime chloride, CHBrPh·CHBr·CCl:N·OEt, prepared by warming the chloride with a slight excess of bromine, is a solid compound readily soluble in ether, benzene, and chloroform, but only sparingly in light petroleum, and insoluble in water.

Phenylallenylphenyluramidethoxime,

CHPh:CH·C(NOEt)·NH·CO·NHPh,

obtained by treating phenylallenylamidethoxime with phenylcarbimide, crystallises from dilute alcohol in colourless needles, melts at 155—156°, and is readily soluble in alcohol, ether, benzene, and chloroform, but only sparingly in light petroleum, hot water, and hydrochloric acid, and insoluble in potash and cold water.

Phenylallenylphenyluramidoxime,

CHPh:CH·C(NOH)·NH·CO·NHPh,

prepared in like manner from phenylallenylamidoxime, crystallises from dilute alcohol in colourless needles, melts at 158—159°, and is readily soluble in ether, but only moderately so in benzene and chloroform, sparingly in light petroleum, and insoluble in cold water; it is only very sparingly soluble in acids and alkalis.

Phenylallenyluramidoxime, CHPh:CH·C(NOH)·NH·CO·NH_2, separates in colourless needles when an aqueous solution of phenylallenylamidoxime hydrochloride is treated with potassium cyanate; it melts at 158—159°, and is readily soluble in alcohol and ether, but only moderately in benzene and chloroform, and sparingly in light petroleum and cold water. It forms salts with acids, and dissolves unchanged in alkalis, but when treated with concentrated acids or alkalis at the ordinary temperature, it is reconverted into the amidoxime. The *platinochloride*, $(C_{10}H_{11}N_3O_2)_2,H_2PtCl_6$, is crystalline.

Ethyl phenylallenylamidoximecarboxylate,

CHPh:CH·C(NH_2):N·O·COOEt,

is obtained, together with the hydrochloride of the amidoxime, when phenylallenylamidoxime (2 mols.) is treated with ethyl chlorocarbonate (1 mol.) in benzene solution. It is a crystalline, unstable compound, melts at 101°, and is readily soluble in ether, alcohol, chloroform, and benzene, but only sparingly in light petroleum, and insoluble in water.

Phenylallenylcarbonylimidoxime, $CHPh:CH\cdot C<\genfrac{}{}{0pt}{}{N——O}{NH\cdot CO}>$, is formed when the preceding compound is warmed with alkalis, or heated above its melting point. It crystallises from dilute alcohol in slender needles, melts at 199—200°, and is readily soluble in alcohol, ether, benzene, and chloroform, but only sparingly in light petroleum, and is insoluble in cold water. It has an acid reaction, and in neutral solutions of the ammonium-derivative, silver nitrate produces a white, and copper sulphate a green precipitate. F. S. K.

Substituted Amidoximes. By H. MÜLLER (*Ber.*, **22**, 2401—2412; compare Abstr., 1886, 875).—Benzenylphenylcarbonylimidoxime, melting at 166—167°, is formed, together with benzylanilidoxime hydrochloride, when benzenylanilidoxime is treated with carbonyl chloride in benzene solution.

Benzenylanilidoxime combines with chloral in the cold, forming a colourless, flocculent compound, $NHPh\cdot CPh:NOH,C_2Cl_3OH$, which melts at 128—130°, is readily soluble in alcohol, ether, chloroform, and benzene, and is decomposed by concentrated acids and boiling water.

Ethylbenzamide, $COPh\cdot NHEt$, prepared by gradually adding benzoic chloride to an ethereal solution of ethylamine in the cold, separates from ether in large crystals, melts at 69—70°, and is soluble in water, benzene, chloroform, and alcohol, but only sparingly in light petroleum; it is moderately easily soluble in hydrochloric acid, but insoluble in soda.

Benzoparatoluidide, $COPh\cdot NH\cdot C_6H_4Me$, prepared from benzoic chloride and toluidine in like manner, crystallises in plates, and melts at 157—158°.

Thiobenzoparatoluidide, $CSPh\cdot NH\cdot C_6H_4Me$, is best prepared by warming the preceding compound with phosphorus pentasulphide; it crystallises from dilute alcohol in long yellow needles, melts at 128—129°, and is readily soluble in alcohol, ether, chloroform, benzene, light petroleum, and soda, but insoluble in water.

Benzenylparatoluidoxime, $NOH:CPh\cdot NH\cdot C_6H_4Me$, prepared by heating thiobenzotoluidine with hydroxylamine hydrochloride and sodium carbonate in dilute alcoholic solution, crystallises from dilute alcohol in long, colourless needles, melts at 176°, and is readily soluble in ether, chloroform, benzene, acids, and alkalis, but only moderately so in hot water. The *hydrochloride*, $C_{14}H_{14}N_2O,HCl$, crystallises in colourless needles, and is sparingly soluble in water.

Benzenylparatoluylcarbonylimidoxime, $C_6H_4Me<\genfrac{}{}{0pt}{}{CPh}{CO}>NO$, prepared by treating benzenyltoluidoxime with ethyl chlorocarbonate in chloroform solution, crystallises from dilute alcohol in yellowish needles, melts at 163°, and is readily soluble in ether, chloroform, benzene, and light petroleum, but insoluble in water, acids, and alkalis.

Ethenylanilidoxime, $NOH:CMe\cdot NHPh$ (m.p. 120—121°), is obtained when thiacetanilide is boiled with an alcoholic solution of hydroxylmine hydrochloride and sodium carbonate. The *hydrochloride*,

$C_8H_{10}N_2O,HCl$, crystallises in colourless needles. The *platinochloride*, $(C_8H_{10}N_2O)_2,H_2PtCl_6$, crystallises in slender, yellow needles. The *benzoyl*-derivative, NOBz:CMe·NHPh, crystallises from dilute alcohol in colourless needles, melts at 110°, and is soluble in benzene, chloroform, and ether, but insoluble in water and light petroleum.

Methenylanilidoxime, NOH:CH·NHPh, prepared in like manner, crystallises from a mixture of benzene and light petroleum in colourless needles, melts at 116°, and is moderately easily soluble in water, alcohol, ether, chloroform, and benzene, but almost insoluble in light petroleum. The *hydrochloride*, $C_7H_8N_2O,HCl$, crystallises in needles. The *platinochloride*, $(C_7H_8N_2O)_2,H_2PtCl_6$, crystallises in yellowish needles. The *benzoyl*-derivative, NOBz:CH·NHPh, crystallises in colourless needles, melts at 144—145°, and is moderately easily soluble in alcohol, ether, chloroform, and benzene, but almost insoluble in water and light petroleum. F. S. K.

Action of Acetaldehyde and of Ethyl Acetoacetate on Benzenylamidoxime. By F. TIEMANN (*Ber.*, **22**, 2412—2417).—*Ethylidenebenzenylamidoxime*, $CPh{<}{}^{NO}_{NH}{>}CHMe$, separates in rhomb-prisms, when an aqueous solution of acetaldehyde (1 mol.) and benzenylamidoxime (1 mol.) is kept for some time in a warm place. It melts at 82°, and is readily soluble in alcohol, ether, acetone, and benzene, but only sparingly in hot, and insoluble in cold water; it is decomposed when heated with acids. The *hydrochloride*, $C_9H_{10}N_2O,HCl$, prepared by passing hydrogen chloride into an ethereal solution of the base, is crystalline. The *platinochloride*, $(C_9H_{10}N_2O)_2,H_2PtCl_6$, is an orange-yellow compound, soluble in alcohol and decomposed by water. The base is converted into benzenylethenylazoxime by potassium permanganate in cold, dilute sulphuric acid solution.

Benzenylacetoethenylazoxime, $CPh{<}{}^{NO}_{-N}{>}C\cdot CH_2Ac$, prepared by heating benzenylamidoxime with ethyl acetoacetate, crystallises from boiling water in short, yellowish prisms, melts at 86°, and is readily soluble in alcohol, ether, benzene, and acetone, but only sparingly in light petroleum and boiling water; it dissolves freely in alkalis, but is insoluble in acids. When boiled with alkalis, it is decomposed into benzenylethenylazoxime and acetic acid. The *oxime*, $C_{11}H_{11}N_3O_2$, crystallises from alcohol in colourless needles, melts at 80°, and is soluble in ether, benzene, and hot water, but almost insoluble in light petroleum and cold water. It is a feeble acid, and reduces Fehling's solution on warming. The *hydrazone*, $C_{17}H_{16}N_4O$, prepared by heating the ketone with phenylhydrazine, crystallises from dilute alcohol in yellowish needles, melts at 126°, and is insoluble in water and light petroleum, but readily soluble in alcohol, ether, benzene, and acetone. F. S. K.

Paranitrobenzenylamidoxime and Paramethylorthonitrobenzenylamidoxime. By J. WEISE (*Ber.*, **22**, 2418—2432).—*Paranitrobenzenylamidoxime*, $NO_2\cdot C_6H_4\cdot C(NH_2)$:NOH, is obtained, together with paranitrobenzamide (m.p. 197°), when paranitrobenzonitrile, prepared from paranitraniline by Sandmeyer's method, is

digested with hydroxylamine hydrochloride and sodium carbonate in aqueous solution. It crystallises in yellow needles, melts at 169°, distils without decomposition, and gives all the reactions of amidoximes; it is moderately easily soluble in alcohol and hot water, but rather sparingly in benzene, ether, and chloroform, and insoluble in light petroleum. The *hydrochloride*, $C_7H_7N_3O_3,HCl$, crystallises from water in colourless, hygroscopic needles, melts at 185° with decomposition, and is soluble in alcohol, but is reprecipitated on adding ether. The *ethyl*-derivative, $NO_2\cdot C_6H_4\cdot C(NH_2)\colon N\cdot OEt$, is obtained by treating the amidoxime with sodium ethoxide and digesting the resulting deep-red solution with ethyl iodide; it is best obtained in a pure state by decomposing the hydrochloride with dilute soda. It forms large, yellow, prismatic crystals, melts at 59—60°, and is readily soluble in alcohol and ether, but only moderately so in benzene, and sparingly in light petroleum and hot water. The *hydrochloride* separates from alcoholic ether in colourless crystals.

Paranitrobenzenylethenylazoxime, $NO_2\cdot C_6H_4\cdot C{<}^{NO}_{N}{>}CMe$, prepared by dissolving the amidoxime in acetic anhydride, crystallises in colourless plates, melts at 144°, and is readily soluble in alcohol, ether, and benzene, but only very sparingly in hot water. The corresponding *benzenyl*-compound, $NO_2\cdot C_6H_4\cdot O{<}^{NO}_{N}{>}CPh$, prepared by warming the amidoxime with benzoic chloride, crystallises from alcohol in small, colourless needles, melts at 198°, and sublimes without decomposition when heated slowly, but explodes when heated quickly. It is insoluble in light petroleum, and only moderately soluble in alcohol, but readily in ether, benzene, and glacial acetic acid.

Ethyl paranitrobenzenylamidoximecarboxylate,

$$NO_2\cdot C_6H_4\cdot C(NH_2)\colon NO\cdot COOEt,$$

is formed when the amidoxime is treated with ethyl chlorocarbonate in cold chloroform solution. It crystallises from cold, dilute alcohol in small needles, melts at 169°, and is moderately easily soluble in alcohol, ether, benzene, and chloroform, but only very sparingly in water, and insoluble in light petroleum.

Paranitrobenzenylcarbonylimidoxime, $NO_2\cdot C_6H_4\cdot C{<}^{NO}_{NH}{>}CO$, is obtained when the preceding compound is boiled with alkalis or heated alone; it separates from alcohol in small, yellow needles, melts at 286°, and is insoluble in light petroleum, and only very sparingly soluble in hot water, but more readily in alcohol, ether, and benzene. It is a very stable compound, and dissolves freely in alkalis; in a neutral solution, copper sulphate produces a green precipitate.

Carbonyldi-paranitrobenzenylamidoxime,

$$CO[NO\colon C(NH_2)\cdot C_6H_4\cdot NO_2]_2,$$

prepared by treating the amidoxime with carbonyl chloride in benzene solution at the ordinary temperature, crystallises in small, yellowish needles, melts at 232°, and is very readily soluble in alcohol,

and moderately so in hot water, but more sparingly in benzene and ether, and insoluble in light petroleum; it is converted into paranitrobenzenylcarbonylamidoxime when warmed with alkalis.

Ethylideneparanitrobenzenylamidoxime, $NO_2 \cdot C_6H_4 < {NO \atop NH} > CHMe$, separates in dark yellow crystals when an aqueous solution of the amidoxime is treated with a slight excess of acetaldehyde and kept for some days; it crystallises in needles, melts at 153°, and is readily soluble in alcohol, ether, benzene, and chloroform, but only sparingly in hot water, and insoluble in light petroleum. It is not acted on by dilute acids or alkalis in the cold, but oxidising agents convert it quantitatively into the azoxime. It is decomposed into its constituents when warmed with dilute hydrochloric acid. A yellow, flocculent compound separates from the solution when ethylideneparanitrobenzenylamidoxime is treated with warm dilute soda. This substance melts at 252°, is very stable, and is insoluble, or only very sparingly soluble in most ordinary solvents. It dissolves unchanged in concentrated sulphuric acid, and is not acted on by reducing or oxidising agents, or when heated at 150° with concentrated hydrochloric acid; it is decomposed by fuming nitric acid, yielding a neutral compound which melts at about 180°, and seems to be a dinitroethenylazoxime.

Chlorethylideneparanitrobenzenylamidoxime,

$$NO_2 \cdot C_6H_4 \cdot C < {NO \atop NH} > CH \cdot CH_2Cl,$$

is formed when the amidoxime is boiled with dichlorethyl ether in aqueous solutions. It crystallises from dilute alcohol in yellow plates, melts at 176°, and is very readily soluble in alcohol, but only moderately easily in benzene, ether, and water, and insoluble in light petroleum. It resembles the preceding compound in its chemical behaviour, and yields a complex condensation-product when warmed with alkalis.

Ethylparanitrobenzenyloxime nitrite, $NO_2 \cdot C_6H_4 \cdot C(NOEt) \cdot O \cdot NO$, prepared by treating the amidoxime with sodium nitrite in cold, dilute sulphuric acid solution, is a yellow, very unstable, flocculent compound melting at 55° with explosive violence; it is soluble in alcohol and ether, but insoluble in water. It decomposes slowly at the ordinary temperature with evolution of oxides of nitrogen, and explodes when heated with water or when treated with concentrated sulphuric acid.

Paranitrobenzenylacetoethenylazoxime, $NO_2 \cdot C_6H_4 \cdot C < {NO \atop N} \geqslant C \cdot CH_2Ac$, is formed when the amidoxime is digested with ethyl acetoacetate. It crystallises from dilute alcohol in golden plates, melts at 140°, and is readily soluble in alcohol and ether, but only moderately so in benzene, very sparingly in water, and insolnble in light petroleum. When heated with alkalis, it is quickly decomposed into acetic acid and nitrobenzenylethenylazoxime.

Paramidobenzenylamidoxime, $NH_2 \cdot C_6H_4 \cdot C(NH_2) \colon NOH$, prepared by reducing the nitro-compound with stannous chloride and hydrochloric

acid and decomposing the resulting salt with sodium carbonate, crystallises in yellow plates, turns brown at 160°, and melts at 174° with decomposition. It is very readily soluble in alcohol, but only moderately easily in benzene and ether, sparingly in hot water and insoluble in light petroleum; it gives the reactions of amidoximes, and dissolves freely in alkalis.

Paramethylorthonitrobenzonitrile, [CN : NO_2 : Me = 1 : 2 : 4], prepared from metanitroparatoluidine by Sandmeyer's method, crystallises from water in long yellowish needles, melts at 99°, distils without decomposition, and is readily soluble in alcohol, ether, benzene, and chloroform, but only sparingly in hot water, and almost insoluble in light petroleum.

Paramethylorthonitrobenzenylamidoxime, $NO_2{\cdot}C_6H_3Me{\cdot}C(NH_2){:}NOH$, is obtained by digesting methylnitrobenzonitrile with hydroxylamine in alcoholic solution, and is best prepared in a pure state by decomposing the copper-derivative with hydrogen sulphide. It crystallises in long, yellow needles, melts at 161°, and shows the properties of an amidoxime; it is moderately easily soluble in alcohol and hot water, but only sparingly in benzene, ether, and chloroform, and is insoluble in light petroleum. The *hydrochloride*, $C_8H_9N_3O_3,HCl$, is a colourless, crystalline compound, soluble in alcohol, but reprecipitated on adding ether.

Paramethylorthonitrobenzamide, [$CONH_2$: NO_2 : Me = 1 : 2 : 4], is formed in the preparation of the preceding compound. It crystallises from water in long, yellow needles, melts at 152°, and is readily soluble in alcohol, ether, and benzene, but almost insoluble in light petroleum; it is converted into the corresponding acid when boiled with alkalis.

Paramethylorthamidobenzenylamidoxime,

$$NH_2{\cdot}C_6H_3Me{\cdot}C(NH_2){:}NOH,$$

is produced in small quantities when methylnitrobenzenylamidoxime is reduced with stannous chloride and hydrochloric acid. It is a brown, flocculent compound, melts at about 166°, and gives the reactions of amidoximes. The *hydrochloride* is a colourless, crystalline, hygroscopic compound soluble in alcohol, but reprecipitated on adding ether.

F. S. K.

Para- and Ortho-homobenzenylamidoxime and their Derivatives. By L. H. Schubart (*Ber.*, **22**, 2433—2440; compare Abstr., 1886, 797).—*Parahomobenzenylethenylazoxime*,

$$C_6H_4Me{\cdot}C{<}{}^{NO}_{-N}{>}CMe,$$

prepared by boiling the amidoxime with acetic anhydride, crystallises in colourless prisms, melts at 80°, and is readily soluble in alcohol, ether, chloroform, and benzene, but insoluble in acids and alkalis.

Parahomobenzenylethoxime chloride, $C_6H_4Me{\cdot}CCl{:}NOEt$, obtained by treating the amidethoxime with hydrochloric acid and sodium nitrite, is a yellow oil, boils at about 200°, and is soluble in alcohol and ether. The corresponding *bromide*, prepared in like manner, is a

heavy, brown oil; it decomposes at 155°, and is readily soluble in ether, chloroform, and benzene.

Parahomobenzenylpropenylazoxime-ω-carboxylic acid,

$$C_6H_4Me{\cdot}C{\lessgtr}^{NO}_{-N}{\gtrless}C{\cdot}C_2H_4{\cdot}COOH,$$

is formed when the benzenylamidoxime is melted with succinic anhydride. It crystallises from boiling water in colourless needles, melts at 138·5°, and is soluble in alcohol, ether, chloroform, and benzene.

Parahomobenzenyluramidoxime, $C_6H_4Me{\cdot}C(NOH){\cdot}NH{\cdot}CO{\cdot}NH_2$, prepared by treating the hydrochloride of the amidoxime with potassium cyanate in aqueous solution, crystallises in colourless needles, melts at 170°, and is readily soluble in alcohol, ether, and benzene, but only sparingly in water. The *thiouramidoxime*,

$$C_6H_4Me{\cdot}C(NOH){\cdot}NH{\cdot}CS{\cdot}NHPh,$$

prepared by treating the amidoxime with phenylthiocarbimide, crystallises from hot water in colourless needles, melts at 190°, and is readily soluble in alcohol and ether, but more sparingly in chloroform and benzene.

Parahomobenzenylphenyluramidoxime,

$$C_6H_4Me{\cdot}C(NOH){\cdot}NH{\cdot}CO{\cdot}NHPh,$$

prepared from phenylcarbimide in like manner, separates from dilute alcohol in colourless crystals, melts at 155°, and is readily soluble in alcohol, ether, and hot water.

Ethyl parahomobenzenylamidoximecarboxylate,

$$C_6H_4Me{\cdot}C(NH_2){:}NO{\cdot}COOEt,$$

is obtained by treating the amidoxime with ethyl chlorocarbonate in chloroform solution; it crystallises from dilute alcohol in colourless needles, melts at 130°, and is readily soluble in alcohol, ether, chloroform, and benzene, but only sparingly in light petroleum and water.

Parahomobenzenylcarbonylimidoxime, $C_6H_4Me{\cdot}C{\lessgtr}^{NO}_{NH}{>}CO$, crystallises from hot water in colourless needles, melts at 220°, and is soluble in ether, alcohol, and alkalis.

Diparahomobenzenylazoxime, $C_6H_4Me{\cdot}C{\lessgtr}^{NO}_{N}{\gtrless}C{\cdot}C_6H_4Me$, is formed when the amidoxime is heated with glacial acetic acid. It crystallises from dilute alcohol in long, colourless needles, melts at 135°, and is insoluble in water, but readily soluble in ether, benzene, chloroform, and light petroleum.

Ethylideneparahomobenzenylamidoxime, $C_6H_4Me{\cdot}C{\lessgtr}^{NO}_{NH}{>}CHMe$, melts at 127·5°, and is readily soluble in alcohol, ether, and benzene, but only sparingly in hot water.

Parahomobenzenylacetoethenylazoxime, $C_6H_4Me{\cdot}C{\lessgtr}^{NO}_{-N}{\gtrless}C{\cdot}CH_2Ac$, pared by treating the amidoxime with ethyl acetoacetate, crystallises

from boiling water in colourless needles, melts at 97°, and is readily soluble in alcohol, ether, and benzene.

Orthohomobenzenylamidoxime, $C_6H_4Me\cdot C(NH_2){:}NOH$, obtained from homobenzonitrile (b. p. 195°), crystallises from hot water in yellowish needles, melts at 149·5°, is readily soluble in alcohol, ether, and benzene, and shows the characteristic reactions of amidoximes.

The *ethyl*-derivative, $C_{10}H_{14}N_2O$, forms colourless prismatic crystals, melts at 140°, and is readily soluble in ether, alcohol, and benzene. The *benzoyl*-derivative, $C_{15}H_{14}N_2O_2$, crystallises from dilute alcohol in needles melting at 145°.

Orthohomobenzenylbenzenylazoxime, $C_6H_4Me\cdot C{<}\genfrac{}{}{0pt}{}{NO}{N}{>}CPh$, prepared by dissolving the benzoyl-derivative (see above) in cold, concentrated sulphuric acid, crystallises in long, colourless needles, melts at 80°, and is insoluble in acids, alkalis, and cold water, but readily soluble in alcohol, ether, benzene, and chloroform. F. S. K.

Action of Carbon Bisulphide on the Potassium Compound of Parahomobenzenylamidoxime. By L. H. Schubart (*Ber.*, **22**, 2441—2442).—A compound $C_9H_8N_2S_2$ is formed when parahomobenzenylamidoxime (1 mol.) is dissolved in alcoholic potash and the solution boiled for about three hours with carbon bisulphide (1 mol.). It crystallises from alcohol in yellow needles, melts at 165°, and is soluble in ether, chloroform, benzene, and alkalis.

The compound $C_8H_6N_2S_2$ can be obtained from benzenylamidoxime in like manner. It crystallises from alcohol in yellow prisms, and melts at 160°. F. S. K.

Xylenylamidoxime and its Derivatives. By E. Oppenheimer (*Ber.*, **22**, 2442—2449).—Xylylonitrile [CN : Me_2 = 1 : 2 : 4], prepared from metaxylidine by Sandmeyer's method, separates from cold dilute alcohol in long, colourless crystals, melts at 23—24°, is volatile with steam, and is readily soluble in alcohol and ether (compare Gasiorowski and Merz, Abstr., 1885, 772).

Xylenylamidoxime, $C_6H_3Me_2\cdot C(NH_2){:}NOH$, is obtained when the preceding compound is heated with hydroxylamine for 5 to 6 hours at 80—85°. It crystallises in colourless needles, melts at 178°, and is readily soluble in alcohol, ether, chloroform, and hot water, but only sparingly in cold water; it gives all the characteristic reactions of amidoximes. The *ethyl*-derivative, $C_{11}H_{16}N_2O$, crystallises in colourless needles, melts at 172°, and is readily soluble in alcohol, ether, chloroform, benzene, and hot water, but only sparingly in cold water. The *benzoyl*-derivative, $C_{16}H_{16}N_2O_2$, separates from dilute alcohol in colourless crystals, melts at 158°, and is only sparingly soluble in water and light petroleum, but readily in alcohol, ether, and chloroform.

Xylenylbenzenylazoxime, $C_6H_3Me_2\cdot C{<}\genfrac{}{}{0pt}{}{NO}{N}{>}CPh$, prepared by heating the benzoyl-derivative described above, crystallises in yellowish scales, melts at 98°, sublimes readily, and is volatile with steam; it is readily soluble in alcohol, ether, chloroform, and benzene.

Acetylxylenylamidoxime, $C_6H_3Me_2\cdot C(NH_2)\colon NOAc$, obtained by treating the amidoxime with acetic chloride in ethereal solution, crystallises from cold alcohol in colourless needles, melts at 189°, and is readily soluble in alcohol and chloroform, but only sparingly in ether. The corresponding *ethenylazoxime*, $C_{11}H_{12}N_2O$, is prepared by heating the amidoxime with acetic anhydride and distilling the product with steam; it separates from alcohol or ether in crystals and melts at 89°.

Xylenylazoximepropenyl-ω-carboxylic acid,

$$C_6H_3Me_2\cdot C{<}^{NO}_{-N}{>}C\cdot C_2H_4\cdot COOH,$$

prepared by fusing the amidoxime with succinic anhydride, crystallises in long, colourless needles, melts at 112°, and is readily soluble in alcohol, ether, benzene, and chloroform; it forms crystalline salts with bases.

Ethyl xylenylamidoximecarboxylate, $C_6H_3Me\cdot C(NH_2)\colon NO\cdot COOEt$, is obtained by treating the amidoxime with ethyl chlorocarbonate in chloroform solution. It crystallises from dilute alcohol in colourless needles, melts at 142°, and is readily soluble in alcohol, ether, and chloroform, but only sparingly in light petroleum; it has feeble basic properties.

Xylenylcarbonylamidoxime, $C_6H_3Me_2\cdot C{<}^{NO}_{NH}{>}CO$, prepared by heating the preceding compound, crystallises from hot water in needles, melts at 182°, and is readily soluble in alcohol and ether; it has acid properties.

The *compound* $C_9H_{12}N_2O,CCl_3\cdot COH$ is formed by the direct combination of its constituents; it separates from a mixture of benzene and light petroleum in crystals, melts at 112°, and dissolves unchanged in alcohol and ether, but is decomposed by water and by dilute acids.

Xylenyluramidoxime, $C_6H_3Me_2\cdot C(NOH)\cdot NH\cdot CO\cdot NH_2$, separates in colourless crystals when the hydrochloride of the amidoxime is treated with potassium cyanate in ethereal solution. It melts at 155°, is readily soluble in ether, alcohol, benzene, and light petroleum, but only sparingly in water; it combines with acids and also, but less readily, with bases. The *phenyl*-derivative,

$$C_6H_3Me_2\cdot C(NOH)\cdot NH\cdot CO\cdot NHPh,$$

crystallises from alcohol in light yellow scales, melts at 138°, and is soluble in alcohol, ether, benzene, chloroform, hot water, and acids.

Xylenylphenylthiuramidoxime, $C_6H_3Me_2\cdot C(NOH)\cdot NH\cdot CS\cdot NHPh$, separates from dilute alcohol in light yellow crystals, melts at 150°, and is soluble in alcohol, ether, benzene, acids, and boiling water, but almost insoluble in alkalis. F. S. K.

Action of Sulphuric Acid and Selenic Acid on Aromatic Compounds. By ISTRATI (*Bull. Soc. Chim.* [3], 1, 480—481).—Finding that the prolonged action of sulphuric acid on benzene produced a sulphonic acid, sulphobenzide, and a franceïn, the author heated selenic acid, sp. gr. 1·4 (100 grams), with pure benzene (50 c.c.)

for 32 hours at 80°; neither selenobenzide nor a franceïn was produced, but after neutralisation of the acid by barium carbonate, a small quantity of a crystalline organic compound, which the author believes to be phenyl selenide (comp. Abstr., 1889, 41), was extracted from the barium salt by hot water. Pentachlorobenzene similarly treated gave a corresponding result. T. G. N.

New Data relating to Franceïns. By ISTRATI (*Bull. Soc. Chim.* [3], 1, 481—487; compare Abstr., 1888, 591).—When sulphuric acid is heated with halogen-derivatives of benzene, it causes the migration of halogen-atoms, and this determines the formation from the initial compound of franceïns whose chlorine values differ. Thus from 1 : 2 : 4-trichlorobenzene, three franceïns resulting from the oxidation of di-, tri-, and tetra-chlorobenzenesulphonic acids are produced, and these are accompanied by a small quantity of 1 : 2 : 4 : 5-tetrachlorobenzene. From 1 : 2 : 4 : 5-tetrachlorobenzene, a franceïn is obtained which is separable into five franceïns of varying solubilities and compositions. Numerous analyses are given. T. G. N.

Franceïn from 1 : 2 : 4 : Trichlorobenzene. By ISTRATI (*Bull. Soc. Chim.* [3], 1, 488—492).—From comparative experiments which he has made as to the formation of franceïns from 1 : 2 : 4-trichlorobenzene, the author finds that the yield of franceïn is dependent on the temperature, and varies inversely as the amount of sulphonic acid remaining in the mixture at the close of the operation. T. G. N.

Action of Heat on a Mixture of Sulphuric Acid and Sulphonic Derivatives. By ISTRATI (*Bull. Soc. Chim.* [3], 1, 492—496).—From experimental observations, the author concludes that when a mixture of excess of sulphuric acid and a sulphonic acid or a sulphonate is heated, regeneration of hydrocarbons with formation of water and of pyrosulphuric acid respectively occur, while sulphobenzide is formed as a condensation-product, and a decomposition of the sulphonic acid into sulphurous anhydride, hydrocarbon, and oxygen determines the formation of a franceïn by the oxidation of unaltered sulphonic acid. T. G. N.

α-Ketoaldehydes. By H. MÜLLER and H. v. PECHMANN (*Ber.*, **22**, 2556—2561).—Benzoylformaldehyde (phenylglyoxal), COPh·COH (Abstr., 1888, 146), is prepared by dissolving nitrosoacetophenone (30 grams) in a 35 per cent. solution of sodium hydrogen sulphite (120 grams) contained in a litre flask. When cold, the whole solidifies to a yellowish crystalline mass, and is then stirred with alcohol and glacial acetic acid (1 c.c.), and after some time filtered by suction. The product (30 or 40 grams at a time) is boiled with 11 parts of 17 per cent. sulphuric acid in a flask fitted with an upright condenser until one quarter of the liquid is boiled off. On cooling, crystals of phenylglyoxal hydrate separate and are purified by crystallisation from boiling water. It dissolves in about 35 parts of water at 20°. When heated with nitric acid (sp. gr. 1·4), benzoylformic acid is formed. When an aqueous solution is treated with phenylhydrazine dissolved in dilute

acid, the *α-hydrazone*, NHPh·N:CPh·COH, separates as a brown, crystalline precipitate which may be obtained from alcohol in yellow plates, melts at 142—143°, and is readily soluble in most solvents. The osazone, $C_{20}H_{18}N_4$, is obtained by heating phenylglyoxal with phenylhydrazine acetate (2 mols.) or, more conveniently, from nitrosoacetophenone and an excess of phenylhydrazine; it is identical with Laubmann's compound from benzoyl carbinol and phenylhydrazine (Abstr., 1888, 366). When the aldehyde is dissolved in aqueous soda and boiled for a few minutes, sodium mandelate is formed. It is probable that in the formation of mandelic acid from benzoylcarbinol (Breuer and Zincke, Abstr., 1880, 645) and from acetophenone dibromide (Engler and Wöhrle, Abstr., 1887, 948) benzoylformaldehyde is formed as intermediate product (compare Zincke, *Annalen*, **216**, 315).

When phenylglyoxal is treated with ammonia, a compound of the formula $C_{22}H_{19}N_3O$ or $C_{22}H_{17}N_2O$ is obtained. This crystallises from dilute alcohol in yellowish-white, lustrous plates, melting at 192—193°, and can be distilled; it is soluble in alkalis, and is not changed by sulphuric acid.

Phenylglyoxal reacts with hydroxylamine, yielding the compound $C_{16}H_{13}N_4O_3$. The latter melts at 219°, dissolves in alkalis, and is precipitated by acids as a white powder which becomes yellow when exposed to light.

Nitrosomethyl paratolyl ketone, C_6H_4Me·CO·CH:NOH, prepared by Claisen's method, crystallises from benzene in colourless needles melting at 100°.

Paratolylglyoxal hydrate, C_6H_4Me·CO·CH(OH)$_2$, is prepared from the above compound in a manner similar to phenylglyoxal. It crystallises from water in white, matted needles, softens at 95°, melts at 100—102°, and is readily soluble in alcohol, ether, and benzene, but less soluble in water and light petroleum. When shaken with benzene containing thiophen, and sulphuric acid, the latter becomes green. The aldehyde behaves towards alkalis like the phenyl-compound, is oxidised by nitric acid (sp. gr. 1·4) to toluylformic acid and by permanganate to paratoluylic acid (m. p. 180°). The *osazone*, $C_{21}H_{20}N_4$, obtained by heating a solution of the aldehyde with an excess of phenylhydrazine acetate for 30 minutes on a water-bath, crystallises in yellow needles melting at 145°.

Naphthyl methyl ketone, $C_{12}H_{10}O$, melts at 51—52°, boils at 300—301°, and when oxidised yields β-naphthoic acid. It is not identical with the compound obtained by Claus and Feiss (Abstr., 1887, 271), but possibly is with Pampel and Schmidt's (Abstr., 1887, 252) compound.

N. H. M.

Isomeric Dinitroparatoluic Acids. By B. ROZAŃSKI (*Ber.*, **22**, 2675—2682).—By nitrating orthonitroparatoluic acid (Abstr., 1888, 1088), two dinitro-derivatives were obtained, and their constitution established from the corresponding dinitrotoluenes.

2 : 5-*Dinitroparatoluic acid* (COOH : NO_2 : Me : NO_2 = 1 : 2 : 4 : 5) is very sparingly soluble in cold water, easily in alcohol and acetone, crystallises in needles, and melts at 188°. The *sodium salt* (with $3H_2O$) forms glistening, yellow scales; the *barium salt*

(with $2\frac{1}{2}H_2O$), small, yellowish-white needles; the *calcium salt* (with $2H_2O$), reddish-brown scales; the *ammonium salt*, lemon-yellow scales; the *silver salt*, a white, amorphous powder; the *copper salt*, a light-green powder; the *mercuric*, *lead*, and *iron salts*, white precipitates.

2 : 3-*Dinitroparatoluic acid* [$COOH : NO_2 : NO_2 : Me = 1 : 2 : 3 : 4$] forms yellowish prisms soluble in alcohol, and melts at 249°. It and its salts are less soluble in most solvents than the 1 : 2 : 4 : 5 acid. The *barium salt* (with $4H_2O$) forms pale-yellow needles; the calcium salt (with H_2O), pale-yellow scales. The other salts are similar to those of the isomeric acid. L. T. T.

Acetometanitrobenzoic Anhydride. By W. H. Greene (*Amer. Chem. J.*, 11, 414—415).—When dry silver metanitrobenzoate is treated with excess of cold acetic chloride and the product poured into water, metanitrobenzoic acid is regenerated; Liebermann's statement (this Journal, 1877, ii, 617) that metanitrobenzoylacetic acid (acetometanitrobenzoic anhydride) is formed is incorrect.

Acetometanitrobenzoic anhydride is, however, obtained by treating sodium or silver metanitrobenzoate with acetic chloride, and extracting the product with ether. It forms colourless needles, which melt at 45°. It is insoluble in water, but the presence of either water or alcohol in the ether used for extraction causes complete decomposition of the anhydride. C. F. B.

Action of Phosphorus Trichloride on Salicylic Acid. By R. Anschütz and W. O. Emery (*Amer. Chem. J.*, 11, 387—392).—When salicylic acid is heated with excess of phosphorus trichloride at 70—85°, and the product distilled, first at the ordinary pressure, to get rid of the excess of phosphorus trichloride, and then under reduced pressure, *salicylophosphorus chloride*, $C_7H_4O_3PCl$, solidifies in the receiver. This melts at 36—37°, boils at 127° under 11 mm. pressure, decomposes under ordinary pressure at about 245°, and is soluble in ether, chloroform, and benzene. With phosphorus pentachloride, or with chlorine, it gives an additive-compound, $C_7H_4O_3PCl_3$, of sp. gr. = 1·5587 at 20° (water at 4° = 1), boiling at 168° under 11 mm. pressure; this compound can also be obtained by the action of phosphorus pentachloride on salicylic acid. With bromine, a similar compound, $C_7H_4O_3PClBr_2$, is obtained, of sp. gr. 1·8852 at 20° (water at 4° = 1), and boiling at 185—188° under 11 mm. pressure. The following are given as the most probable formulæ for salicylophosphorus monochloride and its chlorine additive-product respectively:—

$$C_6H_4<{COO \atop -O-}>PCl \text{ and } C_{10}H_4<{COCl \atop OPOCl_2}.$$

C. F. B.

Constitution of Isoeuxanthone. By C. Arbenz (*Chem. Centr.*, 1889, ii, 73; from *Archiv. Sci. phys. nat. Genève* [3], 21, 375).—Phenylsalicylic acid is converted by nitric acid into the dinitro-derivative, $NO_2·C_6H_4(O·C_6H_4·NO_2)·COOH$, which may be split up into paranitrophenol and paranitrosalicylic acid, proving that both nitro-groups are in the para-position. Sulphuric acid converts the

dinitro-derivative into dinitrodiphenyleneketone oxide, which may be reduced to the diamido-derivative, isoeuxanthone. J. W. L.

Oxidation of Orthocarboxycinnamic Acid. By E. EHRLICH (*Monatsh.*, **10**, 574—577; compare Abstr., 1888, 842).—The author has previously shown (Abstr., 1888, 1306) that in alkaline solution, β-naphthol, when oxidised with a limited quantity of permanganate, gives rise to orthocarboxycinnamic acid, $COOH{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}COOH$; whilst the employment of an excess of the oxidising agent leads to the formation of orthocarboxyphenylglyoxylic acid,

$$COOH{\cdot}CO{\cdot}C_6H_4{\cdot}COOH.$$

The former acid, however, is not to be regarded as an intermediate product, for when a 2 per cent. solution of permanganate is slowly run into a solution of orthocarboxycinnamic acid (10 grams) and potash (10 grams) in water (1 litre), decolorisation ceases when about 80 per cent. of the permanganate theoretically required to convert it into orthocarboxyphenylglyoxylic acid has been added, and the solution contains only orthobenzaldehydecarboxylic acid, $COH{\cdot}C_6H_4{\cdot}COOH$ (yield 50 per cent.), which melts at 98—99°, reduces an ammoniacal solution of silver, and furnishes a compound with phenylhydrazine, melting at 107—108°. The author has not succeeded in his endeavour to obtain orthobenzaldehydecarboxylic acid by the direct oxidation of β-naphthol. G. T. M.

Isomeric Derivatives of Ethylbenzene. By L. SEMPOTOWSKI (*Ber.*, **22**, 2662—2674).—When ethylbenzene is heated to boiling, an equal volume of sulphuric acid added, and then, after cooling, the mass is treated with a small quantity of ice-cold water, only *para-ethylbenzenesulphonic acid* is formed; this crystallises in long, colourless, deliquescent needles, is slightly soluble in water, and has a rough, bitter taste. The *barium salt* (with H_2O) forms colourless, silky needles; the *calcium salt*, silvery scales; the *copper salt* (with $4\frac{1}{2}H_2O$), light-blue, glistening scales, decomposing at 170°; the *cadmium salt* (with $7H_2O$), large, transparent, quadratic plates; the potassium salt (with $\frac{1}{2}H_2O$), micaceous scales, decomposing at 150°. All these salts are soluble in water. The *sulphamide*, $C_6H_4Et{\cdot}SO_2NH_2[Et : SO_2NH_2 = 1 : 4]$, crystallises from alcohol in flat, micaceous prisms, easily soluble in ether, sparingly so in water, and melting at 109°. The constitution was proved by the fusion of the potassium salt with potash, when parahydroxybenzoic acid was formed. With a shorter fusion, *para-ethylphenol*, $C_6H_4Et{\cdot}OH$ was obtained; this forms long needles, which melt at 45—46°, boil at 213—214°, and are sparingly soluble in water.* It is very soluble in alcohol and ether, and its aqueous solution gives a violet-grey coloration with ferric chloride, and a yellowish-white precipitate with bromine-water.

The *metasulphonic acid*, $C_6H_3Et(SO_3H){\cdot}OH[Et : SO_3H : OH = 1 : 3 : 4]$, is formed both at high and low temperatures. It is a

* Probably identical with the α-ethylphenol of Beilstein and Kuhlberg, and of Fittig and Kiesow.—*Abstractor.*

reddish oil, of phenol-like odour and miscible with water. The *barium salt* forms colourless, hexagonal plates, decomposing at 120°; the *potassium salt*, silky needles; the *calcium salt*, colourless needles. On fusion with potash, the acid yields protocatechuic acid, proving the correctness of the constitution given.

Metaparadihydroxyethylbenzene, $C_6H_3Et(OH)_2$ [Et : OH : OH = 1 : 3 : 4], is a liquid boiling at 295° and soluble in water. Its aqueous solution is coloured green by ferric chloride, and this colour passes, on the addition of soda, through blue to claret colour.

Orthobromethylbenzenemetasulphonic acid [Et : Br : SO_3H = 1 : 2 : 3 or 5] was obtained by the sulphonation of bromethylbenzene. Its *barium salt* (with $3H_2O$), forms colourless plates, sparingly soluble in cold water; its *potassium salt* (with $\frac{1}{2}H_2O$), colourless scales; and the *sulphamide*, glistening prisms melting at 104—105°.

Parabromethylbenzeneorthosulphonic acid, similarly formed, yields a crystalline *barium salt* (with $4H_2O$), easily soluble in water. The *potassium salt* forms easily soluble scales, the *sulphonamide* large, micaceous scales, melting at 123—124°.

Barium orthoethylbenzenesulphonate (with H_2O), formed by debrominating the bromine-derivative, forms soluble scales; the *cadmium salt*, long, soluble needles; the potassium salt very soluble, glistening scales.

Barium orthoethylphenolmetasulphonate forms microscopic scales.

Barium meta-ethylbenzenesulphonate (with $2H_2O$), obtained by debrominating the bromine-derivative, forms crystals easily soluble in water; the *potassium salt*, easily soluble scales; the *sulphonamide*, glistening scales melting at 85—86°. When fused with potash, this acid yields *meta-ethylphenol*, which forms a colourless oil liquid at —20°, and boiling at 202—204°.

Barium meta-ethylphenolsulphonate forms easily soluble crystals.

L. T. T.

Disulphones and Trisulphones. By E. FROMM (*Annalen*, **235**, 135—167).—Baumann and Escales (Abstr., 1887, 123) obtained ethylidenediethylsulphone by oxidising α-dithioethylpropionic acid. It is more conveniently prepared by acting on a mixture of acetaldehyde and ethyl mercaptan with zinc chloride. The resulting ethyl mercaptal of acetaldehyde (b. p. 186°) is oxidised by agitation with a solution of potassium permanganate containing sulphuric acid. Ethylidenediethylsulphone melts at 75°, and boils at 320° with decomposition. The bromide melts at 115°. Attempts to obtain substitution-products by the action of alkalis, sodium ethoxide, mercaptan, or aniline on the bromide were unsuccessful (Abstr., 1888, 357). *Ethylidenediethylsulphone chloride*, $CMeCl(SO_2Et)_2$, and sodium phenylsulphinite are formed by the action of benzenesulphonic chloride on ethylidenediethylsulphone and sodium ethoxide. The chloride can be prepared by exposing to direct sunlight for several days an aqueous solution of ethylidenediethylsulphone saturated with chlorine. It is deposited from an aqueous solution in needles which melt at 102—103°. The iodide is prepared by boiling the disulphone with an excess of iodine, the crude product being treated

with a cold solution of sodium hydroxide, then washed with cold water, and finally recrystallised from boiling water. The iodide crystallises in needles and melts at 128—129°; at a higher temperature it gives off iodine.

Diethylsulphonedimethylmethane has been described by Baumann (Abstr., 1887, 123). It can be prepared by the action of methyl iodide on an alkaline aqueous solution of ethylidenediethylsulphone.

Diethylsulphonethylmethylmethane is formed by boiling a mixture of sodium ethoxide, ethyl iodide, and ethylidenediethylsulphone in a flask with a reflux condenser. It forms quadratic crystals, and melts at 76°.

The ethyl mercaptal of propaldehyde is lighter than water, and boils between 196° and 200°. On oxidation with permanganate, it yields propylidenediethylsulphone, $CH_3{\cdot}CH_2{\cdot}CH(SO_2Et)_2$; this crystallises in silky needles and melts at 77—78°. The ethyl mercaptal of isobutaldehyde boils between 200 and 210°; it is lighter than water. *Isobutylidenediethylsulphone* melts at 94° and crystallises in needles; it is almost insoluble in cold water. The ethyl mercaptal of benzaldehyde, $PhCH(SEt)_2$, is lighter than water, and boils with decomposition at 250—255°. *Benzylidenediethylsulphone* melts at 133—134°; it is insoluble in cold water, but is soluble in cold solutions of the alkalis. By the action of sodium ethoxide and methyl iodide, it is converted into diethylsulphonemethylmethane.

Diethylsulphonemethane, prepared by the oxidation of the ethyl mercaptal of formaldehyde (from methylene chloride and sodium ethyl mercaptide) is identical with the disulphone Baumann obtained from ethyl orthothioformate (Abstr., 1887, 124). It is converted into diethylsulphonedimethylmethane (sulphonal) by the action of methyl iodide in the presence of an alkali; this melts at 125—126°. *Diethylsulphonediethylmethane* is more difficult to prepare. It melts at 86—88°. An aqueous solution of diethylsulphonemethane readily absorbs chlorine, forming the dichloride, $CCl_2(SO_2Et)_2$. It crystallises in needles and melts at 98—99°. The corresponding diethylsulphonedibromomethane has already been described by Baumann (*loc. cit.*).

Diethylsulphonedi-iodomethane melts at 176—177°, but begins to turn brown at 170°. It crystallises in needles, and is sparingly soluble in hot water.

Diphenylsulphonemethane, $CH_2(SO_2Ph)_2$, prepared by oxidising the phenyl mercaptal of formaldehyde, crystallises in needles and melts at 118—119°. It is soluble in benzene and hot alcohol. Diphenylsulphonedimethylmethane melts at 128° and is soluble in hot alcohol. The corresponding diethyl-derivative melts at 130—131°, and is sparingly soluble in hot alcohol.

When diethylsulphonedibromomethane (1 mol.) is boiled with phenyl mercaptan (1 mol.) and an aqueous solution of sodium hydroxide (rather more than 3 mols.), phenyl bisulphide and diethylsulphonethiophenylmethane are formed. The former is deposited from the solution on cooling, whilst the latter separates out on acidifying the filtrate; it is washed with cold water and recrystallised from absolute alcohol.

Diethylsulphonethiophenylmethane, $PhSCH(SO_2Et)_2$, crystallises in plates and melts at 86°. It is sparingly soluble in hot water and more readily soluble in a solution of sodium hydroxide. On oxidation by permanganate, *diethylsulphonephenylsulphonemethane*,

$$PhSO_2 \cdot CH(SO_2Et)_2,$$

is produced. This trisulphone melts at 165°. It is less soluble in alcohol than in water, and is precipitated from its aqueous solution by strong acids. The aqueous solution turns litmus red, and decomposes carbonates. W. C. W.

Phenylated Indoles. By W. H. INCE (*Annalen*, **253**, 35—44).—3′-Phenylindole yields a crystalline *picrate* soluble in benzene, ether, acetone, and alcohol, and melts at 105°. The *nitrosamine*, $C_{14}H_{10}N_2O$, forms minute, yellow needles, and melts at 60—61°; it is freely soluble in benzene, acetone, ether, and chloroform, but is insoluble in solutions of caustic alkalis. Phenylacetaldehydemethylphenylhydrazone is formed by the interaction of phenylacetaldehyde and methylphenylhydrazine. The alcoholic solution of this compound is decomposed by an alcoholic solution of hydrogen chloride with deposition of ammonium chloride. The liquid is neutralised with ammonia and evaporated, leaving a residue of impure 1′-3′-*methylphenylindole;* this is purified by solution in ether and distillation in a vacuum. The pure indole dissolves in benzene, alcohol, and ether; its alcoholic solution gives a blue colour to a pine chip moistened with hydrochloric acid. The picrate forms dark brown needles, and melts at 90°. Fischer and Schmidt (Abstr., 1888, 958) pointed out that zinc chloride at 170° converts 3′-phenylindole into 2′-phenylindole. In the same way, zinc chloride at 220° transforms 1′-3′-methylphenylindole into the 1′-2′-methylphenylindole described by Degen (Abstr., 1887, 149).

3′-*Phenyl-β-naphthindole* is obtained by the action of alcoholic hydrogen chloride on the hydrazone produced by the interaction of phenylacetaldehyde and β-naphthylhydrazine; it crystallizes in glistening needles, and melts with decomposition at 211°, is soluble in benzene, alcohol, ether, acetone, and hot light petroleum, and stains a pine chip green. The *picrate* forms reddish-brown needles, melts at 119—120°, and is soluble in benzene, acetone, chloroform, alcohol, and ether. The 3′-phenyl-β-naphthindole is converted into 2′-phenyl-β-naphthindole by treatment with zinc chloride at 130°. 2′-Phenyl-β-naphthindole can be more conveniently prepared by the action of zinc chloride on acetophenone-β-naphthylhydrazone, obtained by the condensation of acetophenone and β-naphthylhydrazine. The hydrazone melts at 150°, but it begins to turn brown at 117°. *β-naphthindole* melts at 129—130°, and is freely soluble in alcohol, ether, and benzene. It forms a crystalline picrate (m. p. 165—166°), which is soluble in benzene and ether.

W. C. W.

Benzidine- and Benzidinesulphone-sulphonic Acids. By P. GRIESS and C. DUISBERG (*Ber.*, **22**, 2459—2474).—*Benzidinesulphonic acid*, $NH_2 \cdot C_6H_4 \cdot C_6H_3(NH_2) \cdot SO_3H$, is formed in small quanti-

ties in the preparation of the disulphonic acid (compare Griess, Abstr., 1881, 428), and it can also be obtained in larger quantity by heating benzidine sulphate for $1\frac{1}{2}$ to 2 hours at 170° with sulphuric acid monohydrate (about 6 parts). It is best prepared by heating benzidine sulphate at 170° for about 24 hours (D.R.-P., No. 44,779). It forms anhydrous crystals, and is very sparingly soluble in boiling water, and practically insoluble in alcohol and ether; it is decomposed when heated, yielding a small quantity of benzidine. The *hydrochloride*, $C_{12}H_{12}N_2SO_3,HCl$, separates from hot, dilute, hydrochloric acid in greyish, nodular, anhydrous crystals, and is decomposed by boiling water. The *barium* salt, $(C_{12}H_{11}N_2SO_3)_2Ba + 5H_2O$, is moderately easily soluble in hot water, and separates on cooling in small needles or plates. The *tetrazo*-compound is obtained when an excess of hydrochloric acid and a slight excess of sodium nitrite are added to an ice-cold alkaline solution of the sulphonic acid. It is readily soluble in water, and combines with phenols, hydroxysulphonic acids, and aromatic hydroxycarboxylic acids in alkaline solution, and with amines and amidosulphonic acids in sodium acetate solution, forming yellow, red, and purple dyes. The compounds obtained with the hydroxycarboxylic acids, phenols, and amines respectively are sparingly soluble; the other dyes are readily soluble in water. They all dye unmordanted cotton wool in an alkaline bath, and generally the shade produced is more distinctly purple than that obtained with tetrazodiphenyl dyes, but not so much so as that produced with tetrazodiphenyldisulphonic acid colouring matters.

Benzidinemetadisulphonic acid (compare Griess, *loc. cit.*) is best prepared by heating benzidine sulphate (1 part) with sulphuric acid (2 parts) at 210° for 36 to 48 hours; the yield of the pure compound is 90 per cent. The azo-compounds derived from the tetrazo-derivative do not dye vegetable fibres as readily as those obtained from the tetrazomonosulphonic acid, but they have a more decided blue shade.

Benzidine is not acted on by fuming sulphuric acid at temperatures below 100—120°, but the azo-compounds obtained from tetrazodiphenyl and naphthylamines react with fuming sulphuric acid in the cold, the hydrogen in the benzidine being substituted.

Benzidinetrisulphonic acid $C_6H_2(NH_2)(SO_3H)_2{\cdot}C_6H_3(NH_2){\cdot}SO_3H + 2H_2O$, is obtained, together with the tetrasulphonic acid, when benzidine sulphate is heated for a long time at 180—190° with sulphuric acid monohydrate, or when a solution of benzidine in a little sulphuric acid monohydrate is heated at 160—170°, poured into fuming sulphuric acid, and heated again until a small portion gives only a slight precipitate when treated with water. The product is poured into water, the solution filtered to separate small quantities of the disulphonic acid, and neutralised with barium carbonate. The barium salt of the trisulphonic acid is readily soluble in cold water, and can be easily separated from the salt of the tetrasulphonic acid, which is only sparingly soluble. Benzidinetrisulphonic acid is precipitated in soft, colourless plates on adding concentrated hydrochloric acid to a moderately concentrated solution of the barium salt. It is readily soluble in cold water, but only sparingly in alcohol, and

is reprecipitated from the alcoholic solution on adding ether; it is completely decomposed when heated. The *barium* salt,

$$(C_{12}H_9N_2S_3O_9)_2Ba_3 + 12H_2O,$$

crystallises in small, colourless prisms, and is precipitated from its concentrated aqueous solution on adding alcohol.

Benzidinetetrasulphonic acid,

$$C_6H_2(NH_2)(SO_3H)_2\cdot C_6H_2(NH_2)(SO_3H)_2,$$

is precipitated in small, colourless needles on adding hydrochloric acid to a concentrated aqueous solution of the barium salt; it is very readily soluble in cold water, and is also soluble in alcohol. The *barium* salt, $C_{12}H_8S_4O_{12}Ba_2 + 8H_2O$, crystallises in colourless needles or prisms, and is very sparingly soluble in hot water and insoluble in alcohol.

Benzidinesulphone, $\begin{array}{l}C_6H_3(NH_2)\\ \mid \\ C_6H_3(NH_2)\end{array}\!\!>SO_2$, is best prepared by gradually adding benzidine sulphate (1 part) to a 20 per cent. sulphuric acid solution of sulphuric anhydride, and heating the mixture on the water-bath until it is free from unchanged benzidine; the product is poured on to ice, and the benzidinesulphone sulphate is separated by filtration and decomposed with soda. It crystallises in very small, yellow, anhydrous needles, melts above 350°, and is almost insoluble in boiling water, and insoluble in alcohol, ether, and benzene. The salts are decomposed by water. The *hydrochloride*, $C_{12}H_{10}N_2SO_2,2HCl$, crystallises from hot, dilute, hydrochloric acid, in which it is moderately easily soluble, in almost colourless plates. The *sulphate*,

$$C_{12}H_{10}N_2SO_2,H_2SO_4 + 1\tfrac{1}{2}H_2O,$$

crystallises in grey or colourless needles or plates, and is only sparingly soluble in hot, dilute sulphuric acid. The *platinochloride* crystallises in small, dark, yellow plates, and is insoluble in water.

A *hydroxybenzidine*, $C_{12}H_{11}N_2\cdot OH$, is formed when the sulphone is heated at 180° with caustic soda; it is a grey compound, very sparingly soluble in water, but readily in soda. The *sulphate* and *hydrochloride* are sparingly soluble in water.

When benzidinesulphone hydrochloride is treated with sodium nitrite in aqueous solution, and the resulting brown, amorphous, tetrazo-compound reduced with stannous chloride and hydrochloric acid, the hydrazine is obtained in small, yellow needles sparingly soluble in water. The latter is decomposed when boiled with copper sulphate solution, yielding a diphenylenesulphonic acid melting at 228°, and identical with the compound obtained by Stenhouse (*Annalen*, **156**, 332) from diphenylene sulphide.

The azo-dyes obtained from benzidinesulphone differ from those of benzidine and benzidinesulphonic acids in possessing a marked blue shade.

Benzidinesulphonesulphonic acid, $SO_3H\cdot C_6H_2(NH_2)\!<\!\begin{array}{l}C_6H_3(NH_2)\\ SO_2\,\rule[0.5ex]{3em}{0.4pt}\end{array}\!>$, is formed, together with the di-, tri-, and tetra-sulphonic acid, when the sulphone is heated with fuming sulphuric acid at temperatures above 100°. The crude product is poured on to ice, and, after keep-

ing for some time, the solution is filtered; the tri- and tetra-sulphonic acids, being readily soluble in cold water, pass into the filtrate, whilst the mono- and di-sulphonic acid, which are only sparingly soluble, remain on the filter. The residue is dissolved in soda, and the monosulphonic acid is precipitated from the filtered solution by adding acetic acid; the disulphonic acid in the filtrate is then precipitated by adding a large excess of hydrochloric or sulphuric acid. Benzidinesulphonesulphonic acid crystallises from hot water, in which it is only sparingly soluble, in small, light-yellow needles, and is almost insoluble in alcohol. The *tetrazo*-derivative is a reddish-brown, amorphous compound; it combines with amines, phenols, and with their carboxylic and sulphonic acids, forming dyes which are of a redder shade, and are much more sparingly soluble than those derived from benzidinesulphonedisulphonic acid (see below). The *calcium* salt, $(C_{12}H_9N_2S_2O_5)_2Ca + 8\frac{1}{2}H_2O$, crystallises in small, yellow needles, and is readily soluble in hot water, but only moderately so in boiling alcohol, and sparingly in cold water. The *barium* salt (with $3\frac{1}{2}H_2O$) crystallises in small, golden needles, and is more sparingly soluble in water than the calcium salt.

Benzidinesulphonedisulphonic acid, $\begin{matrix} C_6H_2(NH_2)(SO_3H) \\ | \\ C_6H_2(NH_2)(SO_3H) \end{matrix}\!\!>SO_2 + 1\frac{1}{2}H_2O$, separates in small, light-yellow needles when a boiling aqueous solution is evaporated. It is moderately easily soluble in hot water, but only sparingly in alcohol, and almost insoluble in cold hydrochloric or sulphuric acid. The *tetrazo*-compound is a light-yellow, voluminous substance; it combines with naphthols and naphtholsulphonic acids, yielding purple to violet dyes, and with naphthylamines and naphthylaminesulphonic acid, forming red or bluish-violet colouring matters. It yields beautiful reddish-violet or indigo-blue azo-dyes (sulphoneazurines) with alkyl- and phenylnaphthylamines. The *calcium* salt, $C_{12}H_8N_2S_3O_8Ca + 7H_2O$, crystallises in yellow needles or plates, and is readily soluble in hot, but only sparingly in cold water, and insoluble in alcohol. The *barium* salt (with $4\frac{1}{2}H_2O$) crystallises in needles or very small prisms, and is insoluble in alcohol, and only very sparingly soluble in boiling water. The *sodium* salt crystallises from hot, concentrated, aqueous solutions in long, yellow needles, and is only sparingly soluble in cold water.

Orthotolidine yields analogous compounds to those obtained from benzidine under the same conditions. *Orthotolidinesulphonic acid* is very sparingly soluble in water, and does not crystallise readily. The *tetrazo*-derivative is readily soluble in water. The *barium* salt loses 4 mols. H_2O when dried at 150°. The *disulphonic acid* crystallises from hot, concentrated, aqueous solutions in small, colourless, needles, and is readily soluble in hot water. The *tetrazo*-derivative is insoluble in water. The salts are moderately easily soluble in water; the *sodium* salt crystallises in cubes (with $4H_2O$), the *calcium* salt in plates (with $5H_2O$), and the *barium* salt in needles (with $3H_2O$).

Tolidinesulphone is a greenish-yellow, amorphous compound, the salts of which are very similar to those of benzidinesulphone (D.R.-P., No. 44,784). F. S. K.

β-Naphthylhydrazine. By F. HAUFF (*Annalen*, **253**, 24—35).—The derivatives of β-naphthylhydrazine bear a close resemblance to the corresponding phenylhydrazine-derivatives. The acetyl-derivative, $C_{10}H_7{\cdot}N_2H_2Ac$, prepared by boiling β-naphthylhydrazine with glacial acetic acid for several hours in a reflux apparatus, forms colourless needles soluble in alcohol, chloroform, and benzene, and melts at 164—165°. *Benzoylnaphthylhydrazine*, $C_{10}H_7{\cdot}N_2H_2Bz$, is obtained on adding benzoic chloride to an ethereal solution of naphthylhydrazine (2 mols.); naphthylhydrazine hydrochloride is precipitated, and the filtrate on being evaporated, and the residue treated with a hot dilute solution of sodium hydroxide to remove unaltered benzoic chloride leaves the hydrazine. When pure it crystallises in needles, melts at 154—155°, and is soluble in hot alcohol, ether, benzene, and chloroform. In order to introduce a second benzoyl-group into the preceding compound, it is necessary to act on it with benzoic chloride at a high temperature. The *dibenzoyl*-derivative, $C_{10}H_7{\cdot}N_2HBz_2$, melts at 162—163°.

β-Naphthylsemicarbazide, $C_{10}H_7{\cdot}N_2H_2{\cdot}CO{\cdot}NH_2$, prepared by the action of potassium cyanate on naphthylhydrazine hydrochloride, is soluble in hot alcohol and acetic acid; it melts at 220° (uncorr.), and resembles the corresponding phenyl-derivative in its chemical properties. It is decomposed by the action of hydrochloric acid in sealed tubes at 140°, yielding naphthazine, which has previously been described by Witt (Abstr., 1887, 153).

β-Naphthylthiosemicarbazide, $C_{10}H_7{\cdot}N_2H_2{\cdot}CS{\cdot}NH_2$, is obtained by boiling an alcoholic solution containing equal parts by weight of naphthylhydrazine hydrochloride and ammonium thiocyanate. This substance melts at 201—202° (uncorr.), and is soluble in hot aniline and alcohol. It is decomposed by hydrochloric acid in sealed tubes at 130—140°, yielding *naphthylthiocarbizine*, $C_{10}H_7N{<}\begin{matrix}NH\\ |\\ CS\end{matrix}$. The carbizine melts at 253—254°, and crystallises in plates. It is soluble in warm alcohol, and forms a crystalline hydrochloride and platinochloride. A violet precipitate is formed when bleaching powder is added to the alcoholic solution of the base.

Naphthylhydrazine naphthylthiocarbazinate,

$$C_{10}H_7{\cdot}N_2H_2{\cdot}CS{\cdot}SH,N_2H_3{\cdot}C_{10}H_7,$$

crystallises in plates and melts with decomposition at 145°. It is soluble in warm alcohol.

Ethyl-β-naphthylhydrazine is prepared by the action of ethyl iodide (2 mols.) on naphthylhydrazine in alcoholic solution. It is a pale-yellow oil, freely soluble in alcohol, ether, benzene, and chloroform. It reduces warm Fehling's solution. The solution in chloroform is slowly decomposed by mercuric oxide, yielding naphthylethylamine.

W. C. W.

Derivatives of β-Naphthylhydrazine. By A. HILLRINGHAUS (*Ber.*, **22**, 2656—2657).—In reference to Hauff's work on this subject (preceding Abstract), the author states that he has also recently

obtained the acetyl-derivative, the semicarbazide, and the thiosemicarbazide. L. T. T.

Derivatives of the Two Isomeric Naphthenylamidoximes By E. Richter (*Ber.*, **22**, 2449—2459; compare Abstr., 1887, 374, also Ekstrand, *ibid.*, 373).—β-Napthenylamidoxime (m. p. 150) is readily soluble in alcohol and ether, but only moderately easily in benzene and chloroform and insoluble in light petroleum. The corresponding α-compound (m. p. 148—149°) resembles the β-derivative in its behaviour with solvents.

Benzoyl-β-naphthenylamidoxime, $C_{10}H_7{\cdot}C(NH_2){:}NOBz$, prepared by heating the amidoxime with benzoic chloride, crystallises from hot alcohol in colourless needles, melts at 179°, and is only sparingly soluble in cold alcohol, ether, benzene, chloroform, and light petroleum, insoluble in water.

Naphthenylbenzenylazoxime, $C_{10}H_7{\cdot}C{\lessdot}\genfrac{}{}{0pt}{}{NO}{N}{\gtrdot}CPh$, is formed when the preceding compound is boiled with water, dilute acids, or dilute alkalis, or when it is treated with concentrated sulphuric acid. It crystallises from dilute alcohol in colourless plates, melts at 116°, and is readily soluble in alcohol, ether, benzene, chloroform, and light petroleum, but almost insoluble in water.

Acetyl-β-naphthenylamidoxime, $C_{13}H_{12}N_2O_2$, crystallises from alcohol or benzene in yellowish needles, melts at 154°, and is only sparingly soluble in ether, chloroform, and light petroleum, and insoluble in water; when boiled with water, or when treated with concentrated sulphuric acid, it is converted into the azoxime melting at 85° (compare Ekstrand, *loc. cit.*).

Ethyl-β-naphthenylamidoximecarboxylate, $C_{10}H_7{\cdot}C(NH_2){:}NO{\cdot}COOEt$, separates from alcohol in colourless needles, melts at 121°, and is readily soluble in alcohol, ether, benzene, chloroform, and acids, but very sparingly in light petroleum, and insoluble in water and alkalis.

β-Naphthenylcarbonylimidoxime, $C_{10}H_7{\cdot}C{<}\genfrac{}{}{0pt}{}{NO}{NH}{>}CO$, crystallises from hot benzene in colourless needles, melts at 216°, and is moderately soluble in alcohol, ether, and chloroform, but sparingly in benzene and hot water. The *sodium*-derivative is crystalline. In an aqueous solution of the ammonium-derivative, lead acetate produces a white, and copper sulphate an apple-green precipitate.

β-Naphthenylamidethoxime, $C_{10}H_7{\cdot}C(NH_2){:}NOEt$, crystallises from dilute alcohol in colourless needles, melts at 74—75°, and is readily soluble in alcohol, ether, benzene, chloroform, light petroleum, and hydrochloric acid, but very sparingly in water, and insoluble in alkalis.

Ethylidene-β-naphthenylamidoxime, $C_{10}H_7{\cdot}C{<}\genfrac{}{}{0pt}{}{NO}{NH}{>}CHMe$, prepared by dissolving the amidoxime in acetaldehyde, crystallises from hot water in colourless needles, melting at 121—122°. It is readily soluble in alcohol, ether, benzene and light petroleum, very sparingly soluble in cold water, and insoluble in acids and alkalis.

Acetoethenyl-β-naphthenylazoxime, $C_{10}H_7\cdot C\!\!<\!\!{}^{NO}_{N}\!\!>\!\!C\cdot CH_2Ac$, is formed by boiling the amidoxime with ethyl acetoacetate; it crystallises from hot water in nacreous plates, melts at 108—109° and is soluble in alcohol, ether, benzene, and chloroform but insoluble in light petroleum.

Acetyl-α-naphthenylamidoxime crystallises from dilute alcohol in colourless needles, melts at 129°, and is insoluble in water, but readily soluble in alcohol, ether, benzene, and chloroform; when treated with concentrated sulphuric acid, or when boiled with water, it is converted into the azoxime (compare Ekstrand, *loc. cit.*).

Ethyl-α-naphthenylamidoximecarboxylate crystallises in colourless needles, melts at 111°, and is readily soluble in alcohol, ether, benzene, and chloroform, but only sparingly in light petroleum, and insoluble in water.

α-Naphthenylcarbonylimidoxime, prepared by boiling the preceding compound with water or alkalis, crystallises from dilute alcohol in colourless needles, melts at 189°, and is readily soluble in alcohol but only sparingly in ether, benzene, and chloroform and insoluble in light petroleum and water. In aqueous solutions of the ammonium-derivative, lead acetate produces a white, and copper sulphate a green precipitate. F. S. K.

Acetyl- and Ethyl-derivatives of Camphonitrophenol. By P. Cazeneuve (*Bull. Soc. Chim.* [3], 1, 467—469; compare Abstr., 1889, 618).—The acetyl-derivative of camphonitrophenol, $C_8H_{14}<\begin{matrix}C\cdot NO_2\\ \| \\ C\cdot OAc\end{matrix}$, after saponification and subsequent saturation with slight excess of hydrogen chloride, gives with ferric chloride a violet-red coloration, which indicates the formation of the compound $C_8H_{14}<\begin{matrix}CH\cdot NO_2\\ | \\ C(OH)_2\end{matrix}$. The ethyl-derivative, $C_8H_{14}<\begin{matrix}C\cdot NO_2\\ \| \\ C\cdot OEt\end{matrix}$, is made by heating sodium camphonitrophenoxide with excess of ethyl iodide in sealed tubes at 120° for three hours; after separation of sodium iodide, the liquid is evaporated to dryness and the residue crystallised from benzene. The compound forms large, colourless, flat crystals, which melt at 54° and decompose on distillation. T. G. N.

Camphonitrophenol Phosphate. By P. Cazeneuve (*Bull. Soc. Chim.* [3], 1, 469—471).—The normal phosphate, $(C_{10}H_{14}NO_2)_3PO_4$, is prepared by boiling camphonitrophenol with phosphorus trichloride for several hours. It exists as an amorphous, yellowish, insoluble substance, which, when heated, decomposes without melting. Nitrophenol forms an analogous compound, $(C_6H_4NO_2)_3PO_4$, with phosphorus pentachloride, only traces of metachloronitrobenzene being simultaneously produced. This reaction confirms the constitution previously given to camphonitrophenol. T. G. N.

Camphonitrophenol Benzoate and Phthalate. By P. Cazeneuve (*Bull. Soc. Chim.* [3], 1, 471—472).—The benzoate, $C_8H_{14}<\overset{C\cdot NO_2}{\underset{C\cdot OBz}{\|}}$ is prepared by the reaction of equal parts of camphonitrophenol and benzoic chloride at 100°; it forms small crystals which are insoluble in water, but soluble in hot alcohol, ether, and benzene; these melt at 131°; and partially volatilise at 150° without decomposing. On saponification with alcoholic potash, it yields potassium benzoate and the compound $C_8N_{14}<\overset{C\cdot NO_2}{\underset{C(OH)_2}{|}}$.

Phthalic chloride by a similar reaction forms a compouud,

$$(NO_2\cdot C_{10}H_{14}O)_2C_6H_4O_2,$$

which melts at 275° with slight decomposition. T. G. N.

Quercetin-derivatives. By J. Herzig (*Monatsh.*, **10**, 561—567; compare Abstr., 1888, 1309).—In a previous communication the author has called attention to the fact that pure xanthorhamnin is not the sole product obtaiued from Persian-berries by the method of Liebermann and Hörmann (Abstr., 1879, 271). It is now shown that besides xanthorhamnin, the berries contain a glucoside of rhamnetin or some unstable molecular compound of the glucosides of rhamnetin and quercetin. This result is in accordance with the fact that Schützenberger obtained two glucosides (α- and β-rhamnin) from Persian-berries. His α-rhamnetin (from α-rhamnin) is evidently identical with rhamnetin, his β-rhamnetin (from β-rhamnin) with quercetin. G. T. M.

Scutellarin, one of the Constituents of Scutellaria lanceolaria. By D. Takahashi (*Chem. Centr.*, 1889, ii, 100.)—The root of *Scutellaria lanceolaria*, one of the labiatæ, is used medicinally in China and Japan. By extracting the root with ether, agitating the ether extract with sodium hydroxide, and acidifying the alkaline solution, a yellow. flocculent substance, *scutellarin*, is obtained. It forms odourless and tasteless, shining, flat, yellow needles, melts at 199—199·5°, is insoluble in cold, little soluble in hot water, very readily soluble in alcohol, ether, chloroform. light petroleum, and carbon bisulphide; soluble in sodium hydroxide and carbonate solutions, but carbonic anhydride is not expelled from the latter. It dissolves in concentrated sulphuric acid with a yellow coloration and water reprecipitates the substance unchanged. It dissolves in nitric acid with red coloration, and in like manner in a solution of sulphuric acid and potassium nitrite. Fehling's solution is not reduced by it, even after boiling with hydrochloric acid. It does not combine with phenylhydrazine; neither silver nitrate nor lead acetate precipitates it from its alcoholic solution, but solutions of lead and copper acetates produce a yellow-red precipitate with the alcoholic solution. When treated with bromine in carbon bisulphide solution, a substance crystallising in yellowish needles is formed; the determination of bromine in it, however, gave unsatisfactory results. The elementary analysis of scutellarin gave figures

which corresponded with the formula $C_{10}H_8O_3$; it contains neither nitrogen nor water of combination. 5 grams of scutellarin produced no effect when administered to a dog in an emulsion of milk and gum arabic. The author believes it to be a phenol, and possibly an isomeride of juglone. J. W. L.

Crystallised Digitalin. By ARNAUD (*Compt. rend.*, **109**, 679—682).—Digitalin prepared by Nativelle's method from the *digitalis* of the Vosges formed very thin, brilliant, white, rectangular lamellæ, which melt at 243°, dissolve in absolute alcohol to the extent of 0·650 part in 100 at 14°, and also, contrary to the statement of Schmiedeberg, dissolve in boiling benzene. When subjected to fractional solution, the melting points of the different fractions varied only between 242° and 245°.

A second quantity prepared by Adrian melted at 245—246°, and when dissolved fractionally in alcohol and benzene the melting points varied only between 243 and 245°, as with the first sample.

Digitalin is a distinct chemical individual, and it is not necessary to denote it by any name such as digitoxin. It seems to be the type of a large group of compounds. C. H. B.

Dihydropyrroline. By F. ANDERLINI (*Ber.*, **22**, 2512—2515).—Dihydropyrroline hydrochloride is decomposed when heated, giving off vapours which colour pine-wood red; it is partially decomposed by concentrated hydrochloric acid at 130—140°. The *aurochloride*, $C_4NH_7,HAuCl_4$, crystallises from cold water in small prisms, melts at 152°, and is slowly decomposed when boiled with water. The *picrate*, $C_4NH_7,C_6H_3N_3O_7$, separates from water in yellow crystals, melts at 156°, and is readily soluble in alcohol and water.

Benzoyldihydropyrroline, C_4NH_6Bz, prepared by heating dihydropyrroline hydrochloride with benzoic chloride at 110°, is an oily liquid, boils at 160—161° (2 mm.), and is miscible with alcohol and ether, but is insoluble in water. It dissolves freely in concentrated hydrochloric acid, yielding a salt which does not crystallise readily.

Benzyldihydropyrroline, $C_4NH_6{\cdot}CH_2Ph$, prepared by treating dihydropyrroline with benzyl chloride, boils at 150°. The *aurochloride*, $C_{11}H_{13}N,HAnCl_4$, crystallises from water in yellow needles melting at 111°. F. S. K.

Derivatives of Alkylpyrrolines. By C. U. ZANETTI (*Ber.*, **22**, 2515—2519; compare Ciamician and Zanetti, Abstr., 1889, 727).—1-Ethylpyrroline boils at 129—130° (762 mm., corr.). The tetrabromide melts at 83° and is converted into ethyl dibromomaleïmide (m. p. 93—94°) by cold nitric acid of sp. gr. 1·49. The *diacetyl-*derivative, $C_4NH_2EtAc_2$, is a crystalline compound, melts at 58—59°, boils at about 183° (29 mm.), and is readily soluble in alcohol, ether, benzene, light petroleum, and warm water.

When the mixture of *c*-ethylpyrrolines, boiling at 150° (compare Ciamician and Zanetti, *loc. cit.*), is treated with acetic anhydride and sodium acetate, an oil is obtained which can be separated by frac-

tional distillation into a portion boiling at 210—235° and a portion boiling at 240—255°. The former is volatile with steam and has the composition and properties of an 1-acetyl-*c*-ethylpyrroline, C_4NH_3EtAc. The latter, after having been boiled with potash and repeatedly distilled in order to free it from 1-acetyl derivatives, solidifies partially when exposed to long continued cold, and can thus be separated into its constituents; the crystalline substance is an acetyl-derivative melting at 42—44°, probably identical with the compound (m. p. 47°) obtained by Dennstedt and Zimmermann from *c*-ethylpyrroline (compare Abstr., 1886, 1043). Both the liquid and the solid compound give a silver-derivative which has the composition $C_8H_{10}NOAg$.

1-*Propylpyrroline*, C_4NH_4Pr, is obtained in small quantities when potassium pyrroline is treated with propyl iodide, but isomerides and other compounds are also formed; it is a colourless oil boiling at 145·5—146·5° (755·8 mm.). F. S. K.

Nitropyrroline-α-carboxylic Acids. By F. ANDERLINI (*Ber.*, **22**, 2503—2506).—*Methyl nitropyrroline-α-carboxylate*,

$$NO_2{\cdot}C_4NH_3{\cdot}COOMe,$$

(m. p. 197°) is formed, together with an isomeride (m.p. 179°) and other nitro-compounds, when finely divided methyl pyrroline-α-carboxylate is gradually added to ice-cold nitric acid of sp. gr. 1·5 and the solution poured into cold water; after neutralising with soda and adding a little sodium carbonate, the solution is extracted with ether. It crystallises from boiling water in colourless needles melting at 197°. The corresponding *acid*, $NO_2{\cdot}C_4NH_3{\cdot}COOH$, obtained by hydrolysing the ethereal salt with potash, crystallises from water with 1 mol. H_2O in light-yellow needles, and is readily soluble in alcohol, ether, and hot water, but only sparingly in benzene and cold water. It loses its water when kept over sulphuric acid under reduced pressure, and the anhydrous crystals melt at 217°.

Methyl nitropyrroline-α-carboxylate (m. p. 179°) is obtained, together with other nitro-compounds, when the alkaline solution from which the isomeride (m. p. 197°) has been extracted is acidified and then extracted with ether. It can be isolated by fractionally crystallising the crude product from water. It separates from dilute alcohol in yellow needles melting at 179°. The corresponding *acid* crystallises from hot water, with 1 mol. H_2O, in light-yellow needles, and is readily soluble in alcohol, ether, and hot water and moderately so in benzene, but only sparingly in cold water. It loses its water when kept over sulphuric acid under reduced pressure, the anhydrous compound melting at 161°.

The mother-liquors from the preceding compound (m. p. 179°) probably contain the third isomeride, which has previously been prepared by Ciamician and Danesi (Abstr., 1882, 875) from dinitropyrocoll, but this compound could not be obtained in a pure condition. They also contain the methyl salt of a dinitropyrrolinecarboxylic acid, $C_4NH_2(NO_2)_2{\cdot}COOMe$; this compound crystallises from water, dilute alcohol, and benzene in light-yellow plates melting at about 115°. F. S. K.

Molecular Weights of the Imidoanhydrides of Pyrrolinecarboxylic and Indolecarboxylic Acids. By G. MAGNANINI (*Ber.*, **22**, 2501—2503). Molecular weight determinations by Raoult's method in naphthalene solution show that the molecular formula of pyrocoll is $C_{10}H_6N_2O_2$, that of tetramethylpyrocoll, $C_{14}H_{14}N_2O_2$, that of diacetylpyrocoll, $C_{14}H_{10}N_2O_4$, and that of the imidoanhydride of α-indolecarboxylic acid, $C_{18}H_{10}N_2O_2$. The depression constant of naphthalene was taken as 82, according to Raoult. F. S. K.

Action of Methyl Iodide on Tetramethyldihydropyridine. By F. ANDERLINI (*Ber.*, **22**, 2506—2511).—Pentamethyldihydropyridine hydriodide is obtained when tetramethyldihydropyridine (b. p. 158°) is treated with methyl iodide (compare Ciamician and Anderlini, Abstr., 1889, 728) The free base boils at 188—190° (45—46°; 7 mm.).

A *base*, $C_{12}H_{21}N$, is formed when pentamethyldihydropyridine is treated with methyl iodide in the cold and the resulting oily hydriodide distilled with potash; the base was not isolated. The *aurochloride*, $C_{12}H_{21}N,HAuCl_4$, crystallises in thin, golden needles melting at 99—99·5°. F. S. K.

Synthesis of Oxypyridine and Piperidine Bases. By A. LADENBURG (*Ber.*, **22**, 2583—2590).—*α-Picolylalkine*,

$$C_5NH_4\cdot CH_2\cdot CH_2\cdot OH,$$

is obtained as a thick brown syrup by the action of formaldehyde on α-picoline and is purified by distillation under 20—30 mm. pressure. It is a colourless syrup, boils at 179° under 25 mm. pressure, dissolves readily in water and alcohol, sparingly in ether; it is rather hygroscopic and can only be dried over fused potassium carbonate; sp. gr. 1·111 at 0°. The *platinochloride*, $(C_7H_9NO)_2,H_2PtCl_6$, crystallises well in prisms very readily soluble in hot water and melts at 170° with effervescence. The *aurochloride* crystallises in well-formed crystals rather sparingly soluble in water.

Vinylpyridine, $C_5NH_4\cdot C_2H_3$, prepared by distilling the above compound under higher pressure or in presence of potash, is a colourless, mobile liquid, very readily soluble in alcohol, ether, and chloroform, &c., but only sparingly in water. It boils with decomposition at 158—159° at the ordinary pressure, but distils without decomposition at 79—82° under 29 mm. pressure; sp. gr. = 0·9985 at 0°. The *platinochloride*, $(C_7H_7N)_2,H_2PtCl_6$, crystallises in needles or large plates, melts at 174° with decomposition, and is rather readily soluble in water. The *aurochloride*, *cadmioiodide*, *bismuth iodide*, and *mercurochloride* crystallise well.

α-Pipecolylalkine, $C_5NH_{10}\cdot CH_2\cdot CH_2\cdot OH$, obtained by the action of sodium and alcohol on picolylalkine, is a colourless crystalline base which melts at 31—32° and boils at 225—228°. It is very hygroscopic and is readily soluble water, alcohol, and ether. It is a strong base and turns red litmus blue. The *platinochloride*, $(C_7H_{15}NO)_2,H_2PtCl_6$, crystallises in splendid, large, transparent crystals, like gypsum, and melts at 158°.

α-Methylpipecolinealkine, $C_5NH_9Me{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, is formed when α-pipecolylalkine dissolved in methyl iodide is treated with methyl iodide and sodium at the ordinary temperature. When the methyl iodide has disappeared, the alcohol is evaporated, the residue repeatedly extracted with ether, the base converted into the hydrochloride, and warmed slightly with sodium nitrite. The nitrosamine which separates is removed by ether. The hydrochloride is then treated with potash and the tertiary base is extracted with ether, and dried with potash. The *aurochloride* is crystalline; the *platinochloride, cadmioiodide*, and *periodide* were also prepared.

Vinylpiperidine, $C_5NH_{10}{\cdot}C_2H_3$ (?), is obtained from pipecolylalkin by the method previously employed for the preparation of tropidine from tropine (*Annalen*, **217**, 118). It is a colourless liquid, boils at 146—148°, is readily soluble in water, and has an odour of tropidine and coniine. The *aurochloride* and *picrate* crystallise well and are rather soluble in water.

α-Picolylmethylalkine, $C_5NH_4{\cdot}CH_2{\cdot}CHMe{\cdot}OH$, is formed in a manner similar to α-picolylalkine from α-picoline and acetaldehyde, and is purified by means of the platinochloride. It is yellowish, boils at 176—181° under 18 mm. pressure, and is readily soluble in water, alcohol, and chloroform, sparingly in ether. The *platinochloride*, $(C_8H_{11}NO)_2,H_2PtCl_6$, crystallises from hot water in small plates which melt at 189° with decomposition; the *aurochloride* crystallises well.

α-Pipecolylmethylalkine, $C_5NH_{10}{\cdot}CH_2{\cdot}CHMe{\cdot}OH$, melts at 47°, boils at 224—226°, and is readily soluble in water, alcohol, and ether, The *platinochloride* melts at 149°. In its properties, the base resembles conydrine, with which it is isomeric. N. H. M.

Hydroxymetadiazines (Hydroxypyrimidines). By E. v. MEYER (*J. pr. Chem.* [2], **40**, 303—304).—Amidomethyldiphenylmetadiazine (Abstr., 1889, 578) melts at 168°, not 172°; it can also be obtained by acting on a mixture of ethyl cyanide and phenyl cyanide with sodium or sodium ethoxide.

Hydroxymethyldiphenylmetadiazine (*loc. cit.*) melts at 250°, not 256°; it can also be obtained by the condensation of benzamidine and ethyl methylbenzoylacetate. By heating it with alkaline potassium permanganate, adding dilute hydrochloric acid to the colourless solution, dissolving the precipitate in weak ammonia, filtering, and again precipitating with hydrochloric acid, a *hydroxydiphenylmetadiazinecarboxylic acid*, $CPh{<}{}^{N=CPh}_{N\cdot C(OH)}{>}C{\cdot}COOH$, is obtained; this crystallises from alcohol in beautiful, pale-yellow prisms melting at 236° with evolution of carbonic anhydride. When heated in a diphenylamine bath at 250° until evolution of carbonic anhydride ceases, it leaves a yellow, crystalline residue, mostly soluble in potash; if the precipitate obtained by adding hydrochloric acid to this potash solution is digested with weak ammonia and crystallised from alcohol, yellowish slender needles, $C_{16}H_{12}N_2O$, which melt at 280·5° (uncorr.), are obtained. These appear to be identical with Pinner's diphenylhydroxypyrimidine (Abstr. 1889, 1008), which melts at 284°.

Hydroxymethylethylmethylmetadiazine, $CMe{<}{}^{N \,=\, CEt}_{N\cdot C(OH)}{>}CMe$, is obtained from acetamidine and ethyl propionylpropionate; it melts at 167·5°, and is isomeric with the hydroxy-base of cyanmethethine melting at 150° (Abstr. 1885, 646). A. G. B.

Pyrimidimes. By A. PINNER (*Ber.*, **22**, 2609—2626; compare Abstr., 1889, 1006).—The formation of the pyrimidines appears to take place in three stages. Employing benzamidine and ethyl acetoacetate as examples, these stages are as follows:—

$$\text{I. } NH{:}CPh\cdot NH_2 + COOEt\cdot CH_2\cdot COMe = NH{:}CPh\cdot NH\cdot CO\cdot CH_2\cdot COMe + EtOH.$$

$$\text{II. } NH{:}CPh\cdot NH\cdot CO\cdot CH_2\cdot COMe = NH{<}{}^{CO\cdot CH_2}_{CPh\,:\,N}{>}CMe\cdot OH = NH{<}{}^{CO\cdot CH}_{CPh:N}{>}CMe + H_2O.$$

$$\text{III. } NH{<}{}^{CO\cdot CH}_{CPh\,:N}{>}CMe = N{<}{}^{C(OH)\cdot CH}_{CPh \,=\!=\, N}{>}CMe.$$

The ethyloxalylacetylbenzamidine already described (Abstr., 1889, 1009) is the first-stage product in the formation of phenylhydroxypyrimidinecarboxylic acid, and may be easily converted into the latter by the action of soda. The compound obtained at the same time and melting at 263° is *phenylhydroxypyrimidinecarboxylbenzamidine*, $N{<}{}^{CPh \,=\!=\, N}_{C(OH)\cdot CH}{>}C\cdot CO\cdot NH\cdot CPh{:}NH$, the benzamidine having reacted with the second carboxyl-group of the acetoxalate. It is converted into the above carboxylic acid by the action of soda. As already noted (*loc. cit.*) the free acid melts with decomposition at 247°; carbonic anhydride being evolved and phenylhydroxypyrimidine is formed.

When benzamidine and ethyl acetomalonate react on one another, one carboxyl-group is separated and the same pyrimidine formed as is obtained from ethyl acetoacetate.

When ethyl acetosuccinate, benzamidine hydrochloride, and sodium hydroxide or potassium carbonate are mixed together, two compounds are obtained melting respectively at 178° and 212°. The former (m. p. 178°) is *ethyl phenylmethylhydroxypyrimidineacetate*,

$$CPh{<}{}^{N\,-\,CMe}_{N{:}C(OH)}{>}C\cdot CH_2\cdot COOEt.$$

It is easily soluble in alcohol, ether, and acetone, sparingly in water, and crystallises in needles. When saponified with soda, it yields *phenylmethylhydroxypyrimidineacetic acid*, which crystallises in needles, melts at 259°, and is soluble in alcohol. The needles crystallising at 212° have the formula $C_{11}H_{10}N_2O_2$ and are probably *succinylbenzimide*, $\begin{matrix}CH_2\cdot CO\\ | \\ CH_2\cdot CO\end{matrix}{>}N\cdot CPh{:}NH$. This compound forms the principal product if caustic soda is used for liberating the benzamidine from its hydrochloride in the reaction, whilst, if potassium carbonate is employed, the pyrimidine is the chief product.

With ethyl acetylglutarate, benzamidine yields *ethylphenylmethylhydroxypyrimidinepropionate*, $CPh\langle{N - CMe \atop N:C(OH)}\rangle C\cdot CH_2\cdot CH_2\cdot COOEt$, which crystallises in needles, is soluble in alcohol, ether, and acetone, and melts at 145°. The *free acid* forms a white powder almost insoluble in water and alcohol and melting at 215°.

When ethyl diacetosuccinate is mixed with benzamidine, ethyl phenylmethylhydroxypyrimidineacetate (m. p. 178°) and *phenylmethylacetonylhydroxypyrimidine*, $CPh\langle{N - CMe \atop N:C(OH)}\rangle C\cdot CH_2\cdot COMe$, are formed. The latter is insoluble in acetone, soluble in alcohol; it crystallises in needles and melts at 215°. The author was unable to obtain the dipyrimidine, $CPh\langle{N - CMe \atop N:C(OH)}\rangle C—C\langle{CMe - N \atop C(OH):N}\rangle CPh$, which he had anticipated, the second acetyl-group appearing always to be separated before the pyrimidine formation set in.

A mixture of ethyl succinylsuccinate and benzamidine yields a substance easily soluble in alcohol and melting at 272° and another almost insoluble in the usual solvents. The former, *tetrahydrophenylhydroxyketoquinazoline*, $\begin{matrix} N:C(OH)\cdot C\cdot CH_2\cdot CH_2 \\ | \quad\quad\quad \| \quad\quad\quad | \\ CPh = N\cdot C\cdot CH_2\cdot CO \end{matrix}$, crystallises in needles. The latter, owing to its insolubility, could not be thoroughly purified, but appears to have the formula $C_{22}H_{16}N_4O_2$ and to be *dihydrodiphenyldihydroxyantetrazine*, $\begin{matrix} N:C(OH)\cdot C\cdot CH_2\cdot C\cdot N = CPh \\ | \quad\quad\quad \| \quad\quad\quad \| \quad\quad\quad | \\ CPh = N\cdot C\cdot CH_2\cdot C\cdot C(OH):N \end{matrix}$. It dissolves in boiling caustic soda yielding a crystalline *sodium-derivative*, $C_{22}H_{14}Na_2N_4O_2 + 4H_2O$.

The amidine of acetonecyanhydrin, $OH\cdot CMe_2\cdot C(NH_2):NH$, yields with ethyl acetoacetate, *hydroxyisopropylmethylhydroxypyrimidine*, $OH\cdot CMe_2\cdot C\langle{N - CMe \atop N:C(OH)}\rangle CH$, crystallising in easily soluble needles and melting at 98°. If ethyl benzoylacetate is employed instead of the acetoacetate, *hydroxyisopropylphenylhydroxypyrimidine*,

$$OH\cdot CMe_2\cdot C\langle{N - CPh \atop N:C(OH)}\rangle CH,$$

is formed. This crystallises in small, glistening prisms, sparingly soluble in water, easily so in the usual organic solvents, and melts at 198°. L. T. T.

Phenylhydrazonelevulinic Anhydride. By F. Ach (*Annalen*, **253**, 44—57). Two compounds are formed by the action of phosphorus pentachloride on phenylhydrazonelevulinic anhydride at 150. One contains 2 atoms of hydrogen less than the anhydride and the second compound is a monochloro-snbstitution-product of the first. The crude product of the reaction is poured into water containing ice. In the course of 24 hours, phenylmethylchloropyridazone is deposited in crystals. The mother-liquor is rendered alkaline and treated with ether to extract the phenylmethylpyridazone. The residue is redissolved in 100 parts of boiling water, to which a small quantity of

hydrochloric acid is added. On cooling, the chloro-substitution-product crystallises out and the base is extracted from the mother-liquor as before. It is finally purified by precipitation as the hydrochloride by passing dry hydrogen chloride through its solution in benzene.

Phenylmethylpyridazone, $CO<\begin{matrix}NPh\cdot N\\CH:CH\end{matrix}>CMe$, is freely soluble in alcohol, ether, chloroform, benzene, and acetone, melts at 81—82°, and has feeble basic properties; its salts are decomposed by water. By the action of sodium on the hot alcoholic solution, a crystalline base is produced which appears to have the composition $C_{22}H_{24}N_4$; this melts at 200° and yields a sparingly soluble platinochloride. The solution in dilute sulphuric acid acquires a violet-blue colour on the addition of chromic or nitrous acid.

Phenylmethylchloropyridazone, $CO<\begin{matrix}NPh—N\\CCl:CH\end{matrix}>CMe$, crystallises in flat prisms and melts at 136—137°. It is freely soluble in hot alcohol, chloroform, benzene, and acetone, and also dissolves in mineral acids, but is reprecipitated unaltered from the acid solutions by water. The nitro-derivative melts at 210—213°. The chlorine is displaced by ethoxyl by the action of alcoholic potassium hydroxide.

Phenylmethylethoxypyridazone melts at 146°, crystallises in flat prisms or plates, and dissolves freely in hot alcohol, benzene, chloroform, acetone, and in hot water, and is also soluble in strong acids. It is decomposed by heating at 125° in sealed tubes with hydrochloric acid, yielding *phenylmethylhydroxypyridazone*. The hydroxy-derivative crystallises in needles and melts at 196°. It is soluble in hot acetone, benzene, and chloroform, in strong mineral acids, and in alkalis. The addition of ferric chloride to the hydrochloric acid solution produces a red-brown coloration, which turns to carmine on dilution. At 170°, hydrochloric acid converts the hydroxy-compound into *phenymethylpyrazolecarboxylic acid*, $\begin{matrix}CMe\cdot CH\\ \| \qquad \\ N—NPh\end{matrix}>C\cdot COOH$. The acid is soluble in hot alcohol, chloroform, benzene, ether, and in strong mineral acids, melts at 165—166°, and decomposes at 200°, yielding phenylmethylpyrazole, $\begin{matrix}CMe\cdot CH\\ \| \qquad \\ N—NPh\end{matrix}>CH$, probably identical with the phenylmethylpyrazole described by Knorr (Abstr., 1887, 601).

Phenylmethylpyrazole melts at 34—36° and boils at 254—255° under 753 mm. pressure. It dissolves freely in ether, alcohol, chloroform, acetone, benzene, and light petroleum. The platinochloride forms orange-coloured, needle-shaped crystals, sparingly soluble in water. The pyrazole is converted into the pyrazoline by the action of sodium on its alcoholic solution. The pyrazoline melts at 73—75° and distils without decomposition. It is soluble in ether, alcohol, and benzene, and gives the characteristic pyrazoline-colour reaction with ferric chloride or chromic acid. W. C. W.

Synthesis of Quinazoline-derivatives. By C. Paal and M. Busch (*Ber.*, **22**, 2683—2702).—The authors have studied the action of orthonitrobenzyl chloride on the sodium-derivatives of form-

anilide and of acetanilide and of some of their homologues. The acetanilides did not give satisfactory results, but with the formanilides the following reactions (where R is an aromatic radicle) take place:—

$$NO_2{\cdot}C_6H_4{\cdot}CH_2Cl + R{\cdot}NNa{\cdot}COH = NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NR{\cdot}COH.$$

On reduction, the product yields quinazoline-derivatives,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NR.COH + 3H_2 = C_6H_4{<}\begin{matrix}N{=}CH\\ \ \ \ \ \ \ |\\ CH_2{\cdot}NR\end{matrix} + 3H_2O.$$

Action of Orthonitrobenzyl Chloride on Sodium Formanilide.—Sodium formanilide is prepared by adding sodium to a benzene solution of formanilide, and then a proportional quantity of orthonitrobenzyl chloride is added. *Orthonitrobenzylformanilide*, $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NPh{\cdot}COH$, is soluble in the usual organic solvents, insoluble in water. It melts at 77°, and forms yellow, monosymmetric plates giving the measurements $a : b : c = 0{\cdot}5477 : 1 : 1{\cdot}085$ and $\beta = 69° 7'$. This formanilide was also obtained by boiling orthonitrobenzylaniline (Lellmann and Stickel, Abstr., 1886, 793) with formic acid. When reduced with zinc and acetic or hydrochloric acid, *phenyldihydroquinazoline*, $C_6H_4{<}\begin{matrix}N{=}CH\\ \ \ \ \ \ \ |\\ CH_2{\cdot}NPh\end{matrix}$, is formed; this crystallises in hexagonal plates, is almost insoluble in water and alkalis, easily soluble in mineral acids, alcohol, ether, &c. It melts at 95° and distils at a very high temperature with partial decomposition. When distilled with zinc-dust, it yields equal quantities of aniline and benzonitrile. Its *sulphate*, $(C_{14}H_{12}N_2)_2,H_2SO_4 + 2H_2O$, crystallises from water in needles, loses water at 70° and melts at 79°; when free from water it melts at 140—143°; the *hydrochloride*, $+ 2H_2O$, forms glistening needles melting at 80°; the anhydrous salt melts at 221°, and is easily soluble in alcohol and ether. The *platinochloride* forms yellow crystals melting at 208°; the *aurochloride* orange scales; the *stannochloride*, $C_{14}H_{12}N_2,HSnCl_3$, flat, white needles or scales melting at 130—134°. When heated with methyl iodide in closed tubes at 100°, the quinazoline yields three derivatives: the *methiodide periodide*, $C_{14}H_{12}N_2MeI,I$, forming glistening, golden-yellow scales melting at 157°; the *methiodide*, $C_{14}H_{12}N_2,MeI$, crystallising in white needles melting at 170°; and a third substance, crystallising in prisms melting at 180°, which appears to be a second isomeric *methiodide*. When oxidised with potassium permanganate, the quinazoline yields *phenylketodihydroquinazoline*, $C_6H_4{<}\begin{matrix}N : CH\\ \ \ \ \ \ \ |\\ CO{\cdot}NPh\end{matrix}$, which crystallises in almost colourless, glistening scales or well-formed rhombic crystals giving the measurements $a : b : c = 2{\cdot}4228 : 1 : 3{\cdot}2742$. It melts at 139° and sublimes without decomposition. No hydroxylamine-derivative or phenylhydrazide could be obtained, but with hydrazine (amidogen) it yields *phenylketohydrazodihydroquinazoline*, $\begin{matrix}CH{\cdot}NPh\\ ||\ \ \ \ \ \ \ \ \ \ \\ N{-}C_6H_4\end{matrix}{>}C{<}\begin{matrix}NH\\ |\\ NH\end{matrix}$; this forms white, glistening needles which melt at 204° and, in small quantities, sublime without decomposition. The *hydrochloride*, $C_{14}H_{10}N_2O,HCl$, crystallises in glistening scales and melts at 213—214°; it loses its

hydrogen chloride at a moderate heat. The *platinochloride* crystallises in yellow needles melting above 300°. When the keto-base is treated in alcoholic solution with sodium, *phenyltetrahydroquinazoline*, $C_6H_4<\begin{matrix}NH\cdot CH_2\\ \vert \\ CH_2\cdot NPh\end{matrix}$, is formed which is soluble in organic solvents, crystallises in white needles, melts at 117°, and distils at a high temperature without decomposition. It is only feebly basic, its salts decomposing on the addition of water. It yields a *hydrochloride*, a crystalline *aceto-derivative*, and a *nitrosamine*. An unstable intermediate product containing the (CH·OH) group appears to be formed along with the tetrahydro-compound, but it could not be isolated. When oxidised with permanganate, the tetrahydro-derivative is reconverted into the keto-compound, but both here and in the original formation of the keto-derivative small quantities of a sparingly soluble nitrogenous, crystalline compound melting at 219° are formed.

Action of Orthonitrobenzyl Chloride on Sodium Formoparatoluide.—The reactions here are similar to those with formanilide. *Orthonitrobenzylformoparatoluide*, $NO_2\cdot C_6H_4\cdot CH_2\cdot N(C_6H_4Me)\cdot COH$, crystallises in pale yellow needles melting at 79°, and is easily soluble in the usual organic solvents. It may also be easily prepared from orthonitrobenzylparatolnidine (Lellmann and Stickel, *loc. cit.*). *Paratolyldihydroquinazoline*, $C_6H_4<\begin{matrix}N{=}CH\\ \vert \\ CH_2\cdot N\cdot C_6H_4Me\end{matrix}$, is easily soluble in alcohol, ether, benzene, and chloroform, sparingly so in light petroleum. It crystallises in glistening, white scales, melts at 120°, and distils with partial decomposition. Distilled with zinc-dust, it yields the amine and nitrile like the phenyl-derivative. The *hydrochloride*, with 2 mols. H_2O, forms flat, white needles and melts at 85°, the anhydrous salt at 251°; the *platinochloride* forms glistening, yellow needles melting at 216°; the *stannochloride*, sparingly soluble needles melting at 165°. Methyl iodide forms two derivatives, namely, the *methiodide*, crystallising in white needles melting at 186°, and green, metallic needles which appear to be the *methiodide periodide*. On oxidation, the base yields *paratolylketodihydroquinazoline*, $C_6H_4<\begin{matrix}N{=}CH\\ \vert \\ CO\cdot N\cdot C_6H_4Me\end{matrix}$, which crystallises in micaceous needles sparingly soluble in boiling water, easily in organic solvents, and melting at 146°. The *hydrochloride* forms white needles melting at 213—214°, and is dissociated by slight rise in temperature; the *platinochloride* forms golden yellow scales melting above 300°. By oxidation, *paraketodihydroquinazolylbenzoic acid*, $C_6H_4<\begin{matrix}N{=}CH\\ \vert \\ CO\cdot N\cdot C_6N_4\cdot COOH\end{matrix}$, is produced as well as the above quinazoline; the acid forms white crystals sparingly soluble in organic solvents, and melting at 320°. The *silver salt* forms a white, flocculent precipitate. *Paratoyltetrahydroquinazoline* crystallises in white needles, melts at 127°, and is easily soluble in chloroform and benzene, sparingly in ether and alcohol. It forms a red *nitrosamine*, a white, unstable *hydrochloride*, and a yellow, unstable platinochloride.

Action of Orthonitrobenzyl Chloride on Sodiumformo-orthotoluide.—The reactions are similar to those with the isomeric para-compound.

Orthonitrobenzylformo-orthotoluide forms a yellow oil which melts at 76° and decomposes on distillation. *Orthotolyldihydroquinazoline* forms a yellow, amorphous mass, its *platinochloride* orange-yellow needles melting at 210°, and its *stannochloride* and *hydrochloride* could not be obtained in a crystalline form. When reduced in alcoholic solution with sodium, the base appears to yield the *tetrahydro*-derivative but this was not obtained in a pure state. L. T. T.

Hydrastine. By W. KERSTEIN (*Chem. Centr.*, 1889, ii, 91, from *Zeit. Naturwiss. Halle*, **61**, 425—429).—According to the author's experiments, hydrastine, obtained from the root of *Hydrastis canadensis*, has the formula $C_{21}H_{21}NO_6$, and forms colourless needles melting at 132°. The *hydrochloride*, $C_{21}H_{21}NO_6,HCl$, and *hydrobromide*, $C_{21}H_{21}NO_6,HBr$, are white, micro-crystalline salts; the *hydriodide* is brownish-yellow.

In addition to those reactions already described, showing the relation which exists between hydrastine and narcotine, the author finds that by oxidation with potassium permanganate in acid solution, opianic acid and probably also cotarnine are formed. When distilled in a current of steam, meconine and trimethylamine are formed in the case of both these alkaloïds. On the other hand, they do not show any similarity in their behaviour towards acetic anhydride, acetic chloride, water under pressure, or dilute sulphuric acid.

From hydrastine ethiodide, by the action of potassium hydroxide solution, *ethylhydrastine* is obtained; it forms lemon-yellow crystals which melt at 127°. By the action of iodine, hydrastine is split up into opianic acid and hydrastonine; the latter is distinguished from tarconine methiodide in that no formaldehyde is formed on boiling its iodide or hydroxide with barium hydroxide.

In addition, from the root of *Hydrastis canadensis*, the author has separated *phytosterin*, $C_{26}H_{44}O + H_2O$; this forms plates, melting at 133°, the solution of which in acetic anhydride gives a red coloration, passing into intense blue with concentrated sulphuric acid.

J. W. L.

Formation of Optically Active Tropic Acids and Optically Active Atropines. By A. LADENBURG and C. HUNDT (*Ber.*, **22**, 2590—2592).—A dilute aqueous alcoholic solution of quinine (1 mol.) was added to a hot aqueous solution of tropic acid (m. p. 116—118°, 1 mol.), and the whole evaporated down on a water-bath until crystallisation commenced. On cooling, a quantity of dull, white crystals separated (quinine dextrotropate), and on further evaporation of the mother-liquor an oil separated, which gradually solidified to hard crystals of a glassy lustre (quinine lævotropate).

Quinine dextrotropate melts at 186—187°. The *free acid* crystallises from ether in hard, clear prisms, and from water in clear plates, melts at 127—128°, and showed a rotatory power of 71·4°.

Quinine lævotropate was not obtained quite pure; it melts at 178°. The *free acid*, which was also not obtained pure, melted at 123°, and showed a rotatory power of 65·15°.

When treated with tropine and tropic acid (*Annalen*, **206**, 274), both acids yield the corresponding atropines.

Dextro-atropine crystallises from alcohol in white, lustrous needles, melts at 110—111°, and has a rotatory power of + 10°. The *aurochloride* forms dull, deep-yellow crystals melting at 146—147°.

Lævo-atropine is a crystalline powder melting at 111°. The *aurochloride* crystallises in lustrous needles and melts at 146°. The base resembles hyoscyamine, but the two are not identical, which is due to the fact that the latter base has two active asymmetrical carbon-atoms, whilst the former has only one. N. H. M.

Bases contained in the young Shoots of Solanum Tuberosum. By R. Firbas (*Monatsh.*, **10**, 541—560).—The two products, the one crystalline and the other amorphous, obtained in the preparation of solanine from the young shoots of the potato, are now shown, contrary to earlier views, not to be chemically identical. The author names the crystalline compound *solanine*. It has the formula $C_{52}H_{93}NO_{18},4\frac{1}{2}H_2O$, and when dried at 100° appears to be anhydrous, or to contain only half a molecule of water of crystallisation. From a solution in 85 per cent. alcohol, it crystallises in colourless needles, which melt at 244°, are almost insoluble in ether and alcohol, and are readily dissolved by dilute hydrochloric acid. *Solanidine hydrochloride*, $3(C_{40}H_{61}NO_2,HCl)HCl + H_2O$ or $1\frac{1}{2}H_2O$, is obtained by boiling solanine with a 2 per cent. solution of hydrochloric acid. It is a slightly yellow powder which is only very sparingly soluble in water, and carbonises without melting when heated to 287°. Simultaneously with solanidine hydrochloride, a sugar is formed in accordance with the equation $C_{52}H_{93}NO_{18} = C_{40}H_{61}NO_2 + 2C_6H_{12}O_6 + 4H_2O$.

The amorphous substance obtained simultaneously with solanine, and which the author names *solaneïne*, has, when dried at 100°, the formula $C_{53}H_{87}NO_{13}$, or $C_{52}H_{83}NO_{13}$. The loss of weight on heating the air-dried compound at 100° corresponds with the formula $C_{52}H_{83}NO_{13} + 3\frac{3}{4}$ or $4H_2O$. It is a yellow, horny, perfectly amorphous substance, melting at 208°, is more soluble in an 85 per cent. solution of alcohol than is solanine, and on treatment with hydrochloric acid yields solanidine and a sugar in accordance with the equation $C_{52}H_{83}NO_{13} + H_2O = C_{40}H_{61}NO_2 + 2C_6H_{12}O_6$.

The sugar obtained by the hydrolysis of solanine and solaneïne forms a yellow, amorphous mass with a caramel-like odour, dissolves readily in water and wood-spirit, and has a specific rotatory power of $[\alpha]_D = +28{\cdot}623$. With phenylhydrazine hydrochloride and sodium acetate in aqueous solution, it forms a glucosazone melting at 199°, and resembling the compounds obtained similarly from dextrose, levulose, and several other sugars. With nitric acid it gives no recognisable trace of mucic or saccharic acids. The general behaviour of the sugar points to the conclusion that it is some other sugar than dextrose, or a mixture of sugars.

Solanidine has the formula $C_{40}H_{61}NO_2$ or $C_{41}H_{65}NO_2$, and is obtained from alcoholic solution in amorphous masses interspersed with needles melting at 191°. It dissolves readily in hot alcohol, with difficulty in

ether, and on treatment with excess of dilute sulphuric acid forms a sulphate, $3(C_{40}H_{61}NO_2,H_2SO_4),H_2SO_4 + 8H_2O$; this crystallises in scaly plates melting at 247°, and is readily soluble in water. Its diacetyl-derivative, $C_{40}H_{59}O_2NAc_2$, crystallises in needles melting at 203°. G. T. M.

Cinnamylcocaïne from Coca Leaves. By C. LIEBERMANN (*Ber.*, **22**, 2661—2662).—Measurements of crystals and quantitative decomposition determinations are given to show that the cinnamylcocaïne which the author prepared synthetically from ecgonine is identical with that obtained by Giesel from the coca leaf. L. T. T.

Hæmatoporphyrin and Bilirubin. By M. v. NENCKI and A. ROTSCHY (*Monatsh.*, **10**, 568—573; compare Abstr., 1888, 304 and 971).—The authors suggest that Raoult's method may be employed with advantage to determine the molecular weights of unstable substances of organic origin, and have investigated the practicability of the method in two cases. Making use of acetic acid and phenol as solvents, hæmatoporphyrin gave numbers varying between 226 and 331, which correspond with the simple formula $C_{16}H_{18}N_2O_3$ (mol. wt. = 286). In the case of bilirubin, ethylene dibromide and phenol were used as solvents. This compound has the same molecular formula, and is consequently isomeric with hæmatoporphyrin. The range in the numbers obtained in both cases is due to the compounds being only slightly dissolved by the solvents employed. The isomerism of hæmatoporphyrin and bilirubrin is confirmed by the fact that on reduction with tin and hydrochloric acid two different urobilins are obtained. G. T. M.

Chemistry of Vegetable Physiology and Agriculture.

Reduction of Nitrates by the Cholera Bacteria. By R. J. PETRI (*Chem. Centr.*, 1889, ii, 45, from *Centr. Backteriologie u. Parisitenkunde*, **5**, No. 17).—The cholera bacteria are found to reduce nitrates to nitrites, and the author remarks that an oxidation of ammonia by these bacteria would therefore appear highly improbable. J. W. L.

Mucous Fermentation. By E. KRAMER (*Monatsh.*, **10**, 467—505).—Mucous fermentation is the process by which certain solutions of sugars or carbohydrates, such as saccharose, glucose, lactose, mannitol, starch, and mucilage, containing the necessary quantity of albuminoïds and mineral salts, are converted into a ropy condition. In the process a mucous substance of the formula $C_6H_{10}O_5$ is generally formed simultaneously with variable quantities of mannitol and carbonic anhydride, although in the fermentation of milk the produc-

tion of all these compounds has not been determined with certainty. The formation of free hydrogen and of lactic and butyric acids in ropy fermention is due to the use of impure cultures, and is not the result of the mucous ferment, which is a micro-organism belonging to the bacteria. Previously the mucous fermentation was considered to be due to Pasteur's so named *Micrococcus viscosus* (which, however, does not exist as described by him), but is now shown, in the case of ths different solutions investigated, to be the result of the action of at least three totally different micro-organisms. It also appears that no true mucous fermentation is brought about by Prazmowsky's *Leuconostoc mesenterioïdes* and *Bacillus polymyxa* or by Cohn's *Ascococcus Billrothii.*

The solutions of carbohydrates which have been investigated can be classed into three divisions according to the nature of the ferment capable of producing change in them. The first division consists of neutral or slightly alkaline solutions containing saccharose, albuminoïds, and mineral salts, such as decoctions of barley, of rice, and of maize, to which saccharose has been added; and the juice of the carrot, beet-root, and onion. The fermentation is produced by Kramer's *Bacillus viscosus sacchari*, and affects the saccharose. To the second division belong acid solutions (for example, wine) containing the albuminoïds and mineral salts and glucose. In these the fermentation is caused by Kramer's *Bacillus viscosus vini.* The third division consists of nearly neutral—acid or alkaline—solutions containing lactose, albuminoïds, and mineral salts, such as milk. This class is said by Schmidt-Mülheim to be fermented by a coccus 1 μ in diameter, and capable also of fermenting mannitol.

Kramer's *Bacillus viscosus sacchari* occurs in the form of short rods slightly rounded at the ends, and having a thickness of 1 μ and a length of from 2·5 to 4 μ. They are often joined together, forming strings of as many as 50, and show no individual movement, but only Brown's so-called "molecular motion." When placed on slices of carrot, a blackish mucus is formed, but on isinglass or gelatin made up with saccharose, it produces spreading white colonies; it liquifies the gelatin, and is very active at 22°. The coccus thrives only in neutral or slightly alkaline fluids, producing no change whatever when free acids are present. Kramer's *Bacillus viscosus vini* forms rods 0·6 to 0·8 μ in thickness, and from 2 to 6 μ in length, often occurring in chains 14 μ in length; and belongs to the anaërobic bacteria, whilst the previously described ferment is aërobic. It can only exist in wines or in acid solutions of glucose.

The mucous substance of the formula $C_6H_{10}O_5$ may be regarded as "metamorphosed" cellulose. It is precipitated from the fermented liquid by alcohol, by basic lead acetate, and by baryta-water, in the form of a white, insoluble, amorphous, stringy mass, which has a specific rotatory power of $[\alpha]_D = + 195$; is not coloured by iodine, and is dissolved by solutions of the caustic alkalies, forming a yellow liquid, from which alcohol precipitates a compound as a white, scaly mass. The mucous substance is not to be regarded as being directly produced from the nourishing fluid, but as a secondary product of assimilation of the ferment. Similarly the formation of mannitol is to be attributed to

the action of the nascent hydrogen and carbonic anhydride, the primary products of the action of the living organism on the dissolved glucose. G. T. M.

Decomposition of Albumin by Anaërobic Ferments. By M. v. NENCKI (*Monatsh.*, **10**, 506—525).—The author has investigated the decomposition of serum albumin by three anaërobic bacilli, namely, *Bacillus liquefaciens magnus*, *Bacillus spinosus*, and the *Rauschbrand bacillus*. The fermentations were conducted in a specially arranged flask, and in an atmosphere of nitrogen, hydrogen, or carbonic anhydride. On distillation, after saturation with oxalic acid, the fermented liquid gave gaseous products and liquid fatty acids. On exhaustion with ether, the evaporated residue furnished, besides a small quantity of fatty acids, only phenylpropionic acid, parahydroxyphenylpropionic acid, and scatolacetic acid. The relative quantity in which these three acids are formed depends on the bacillus used and on the length of the fermentation.

Scatolacetic acid, $C_6H_4<\substack{CMe \\ NH}>C\cdot CH_2\cdot COOH$, crystallises from hot water in prisms or six-sided plates, dissolves readily in alcohol and ether, melts at 134° (uncor.), and on treatment with potassium nitrite and acetic acid forms a yellow, crystalline magma of the characteristic nitroso-compound, $C_9H_7N(NO)\cdot C_2H_3O_2$, which melts with decomposition at 135°. Taking these results into consideration, the author shares Salkowski's opinion that there are at least three aromatic groups in albumin, and that these are represented by (1) tyrosine, $OH\cdot C_6H_4\cdot CH_2\cdot CH(NH_2)\cdot COOH$, (2) phenylamidopropionic acid, and (3) scatolamidoacetic acid. When the anaërobic fermentation takes place in the absence of hydrogen, tyrosine is reduced to ammonia, and parahydroxyphenylpropionic acid; phenylamidopropionic acid to phenylpropionic acid, and scatolamidoacetic acid to scatolacetic acid. In the presence of air, these three acids furnish oxidation-products, which may be regarded as being produced as follows:—Phenylacetic acid, benzoic acid, and phenylethylamine from phenylpropionic acid; parahydroxyphenylacetic acid, paracresol, parahydroxybenzoic acid, and phenol from parahydroxyphenylacetic acid, and scatolecarboxylic acid, scatole and indole from scatolacetic acid. G. T. M.

Gases Evolved during the Putrefaction of Serum Albumin. By M. v. NENCKI and N. SIEBER (*Monatsh.*, **10**, 526—531).—The bad smelling gas evolved during the putrefaction of albumin by *Bacillus liquefaciens magnus* (compare preceding abstr.) contains 97·1 per cent. of carbonic anhydride, hydrogen sulphide, and other gases absorbable by potash, and 2·63 per cent. of free hydrogen. The putrid smell is due in all probability to the presence of methyl mercaptan, for the author has proved that that compound is evolved during the putrefaction of flesh by the *Emphysem bacteria*. G. T. M.

Formation of Paralactic Acid during the Fermentation of Sugar. By M. v. NENCKI and N. SIEBER (*Monatsh.*, **10**, 532—540.)—In the preparation of a pure culture of the *Rauschbrand bacillus*, the

authors observed that the fluid taken from the swelling on an inoculated guinea-pig contained not merely the organism which until now was the sole recognised bacillus producing the symptoms, but also an anaërobic micrococcus. The coccus has on the average a diameter of 0·6 μ, but possesses no very characteristic form; appearing usually in a shape resembling that of *diplococcus*, more seldom in strings of 3, 4, or 5, and at times in groups resembling *staphylococcus*. The authors name the new ferment *micrococcus acidi paralactici*, because, during its growth, it converts grape sugar into sarco- or para-lactic acid. The *Rauschbrand bacillus*, on the other hand, converts sugar into the ordinary lactic acid of fermentation, out of which butyric acid is then formed, with evolution of carbonic anhydride and hydrogen. If in fermenting sugar a culture containing both the bacillus and the micrococcus is employed, lactic and paralactic acids are simultaneously formed. G. T. M.

Function of Ammonium Salts in the Nutrition of Higher Plants. By A. MÜNTZ (*Compt. rend.*, **109**, 646—648).—Soil free from nitrates was mixed with ammonium sulphate, and the mixture carefully sterilised. It was then sown with various plants, every precaution being taken to prevent the introduction of the nitric ferment either at this stage or subsequently. A corresponding set of experiments was made in which the nitric ferment was present. In the latter case a considerable quantity of the ammonium sulphate was nitrified. In the first case no nitrates were present at the close of the experiments, and yet the plants flourished vigorously. The quantities of nitrogen in the seeds and the plants were as follows:—

	In the seed.	In the plant.	Derived from the ammonium sulphate.
Broad-bean..	37 mgr.	956 mgr.	915 mgr.
Horse-bean..	16 „	105 „	89 „
Maize......	3 „	211 „	208 „
Barley......	·0·7 „	50 „	49·3 „
Hemp......	0·5 „	115 „	114·5 „

It is evident that the higher plants have the power of directly utilising the nitrogen of ammonium salts, and that preliminary nitrification is not essential. C. H. B.

Fixation of Nitrogen by Leguminosæ. By E. BRÉAL (*Compt. rend.*, **109**, 670—573; compare Abstr., 1888, 1330).—Spanish beans were grown in a mixture of river gravel, fine sand, and flints, which contained very little nitrogen. They were freely exposed to air, and from time to time were watered with very dilute solutions of potassium chloride and calcium phosphate. In March, the roots were inoculated with bacteria from tubercles on the roots of *Cystisu*. At first the growth was vigorous, then the plants languished, but in June they recovered, flourished, and reached maturity. The total gain of nitrogen was 1·4872 gram for a total weight of dried plants of 64·3 grams. At the same time the 10 kilos of gravel, &c., gained

0·481 gram, corresponding with a gain of 98·31 kilos. per hectare of surface exposed.

Lucerne growing in a pot in sandy soil was inoculated with a fragment of tuberculous root of lucerne, freely exposed to air, and watered with effluent water. The total nitrogen in the water used did not exceed 0·1 gram, and the net gain of nitrogen was 3·258 gram for a total weight of dried crop, including roots, of 97·8 gram. At the same time the soil gained 2·460 grams.

This behaviour of the leguminosæ when growing on soils very poor in nitrogen explains their well-known utility as "improving crops."

C. H. B.

Investigations on Lactarius Piperatus. By R. CHODAT and P. CHUIT (*Chem. Centr.*, 1889, ii, 144, 145, from *Arch. sci. phys. nat.*, *Genève*, **5**, 385—403).—After expressing the juices of *Lactarius piperatus*, and extracting the residue with alcohol, it was found that mannitol, a white, crystalline acid, lactaric acid, and a pitchy substance had dissolved. The latter has been named *piperon*. It is solid at ordinary temperatures, but melts on the hand, and has the pepper-like smell of the fungus. Heated with water in the presence of either a little alkali or acid, it remains unchanged. It contains no nitrogen, and is present in the milk of *L. piperatus*.

Lactaric acid, $C_{15}H_{30}O_2$, the next lower homologue to palmitic acid (which has been found by Thoerner in other fungi), melts at 69·5—70°, is little soluble in cold alcohol, readily soluble in hot. It exists in the free state in this fungus to the extent of 7·5 per cent. of the dry substance. The authors could not find any poisonous substance in this fungus either by chemical or physiological means.

J. W. L.

Pectic Compounds in Plants. By L. MANGIN (*Compt. rend.*, **109**, 579—582).—Pectic compounds, both neutral and acid, are essential constituents of plant structures. Their presence is recognised by means of certain dyes, such as phenosafranin, methylene blue, Bismark brown, Paris violet, &c., which stain the pectic compounds but do not stain the cellulose, provided that they are used in neutral solutions or in solutions feebly acidified with acetic acid. Nitrogenous compounds, lignin, and cutin are stained by the same dyes, but on treatment with acid the pectic compounds are decolorised, whilst the others remain stained. Other dyes, such as acid green, acid brown, nigrosin, indulin, crocein, ponceaux, in neutral solution stain the nitrogenous substances, lignin, cutin, &c., but not the pectic compounds, and mixtures of these dyes with those of the first group make excellent double stains, which readily distinguish pectic compounds from lignin, cutin, and the nitrogenous compounds. The author has extracted pectic acid from plant structures which take the stain, and has found that after its removal they remain colourless if treated with the same dyes.

If a section of any plant, except a mushroom, is treated for 24 hours with Schweizer's reagent, the cells are filled with a gelatinous mass enclosed in the cell walls left intact by the section-cutter. It would seem that the cellulose does not diffuse across the membranes, and

after the sections are washed with water and acetic acid, they have their original structure, although somewhat deformed, and the membranes retain their thickness except in those rare cases where the cell walls consist exclusively of cellulose. After this treatment, the cell walls, which consist of insoluble pectic acid, give no coloration with the ordinary iodine reagents, whilst the contents of the cells become deep blue. On the other hand, the cell walls are deeply stained by methylene blue, whilst the contents remain colourless. The cell walls dissolve readily in ammonium oxalate solution.

Pectic compounds are constant constituents of the cell membranes, and are found, though less frequently, in the cell contents, and even in some cases (*Allium porrum*, *Glyceria aquatilis*) in the nucleus.

C. H. B.

The Atmosphere in Soils. By T. SCHLOESING, Junr. (*Compt. rend.*, **109**, 618—620, 673—676).—The large volume of air withdrawn from the soil in Boussingault's method introduces several errors. The author withdraws about 15 c.c. through a steel tube of very narrow diameter, and analyses it volumetrically. The air was drawn from the soil, as a rule, at two depths, 25 to 30 cm., representing the true soil, and 50 to 60 cm., representing the subsoil. It consisted of nitrogen, oxygen, and carbonic anhydride, without any measurable quantity of any combustible gas. The proportion of carbonic anhydride in the soil varied from 0·45 to 11·39 per cent., and in the subsoil from 0·0 to 8·80 per cent.; the proportion of oxygen varied from 13·52 to 20·09 per cent. in the soil, and from 13·21 to 20·98 in the subsoil. As a rule, a low proportion of carbonic anhydride is accompanied by a high proportion of oxygen and *vice versâ*. The greater the depth, the greater, as a rule, the proportion of carbonic anhydride, but in one set of samples taken in June, when the air was calm and the temperature high, this law did not hold good. The atmosphere of the same soil shows great variations, owing doubtless, to the varying frequency with which it is renewed in consequence of changes in the atmospheric pressure. Other conditions being constant, the composition of the atmosphere in the soil will show considerable variations in different parts of the same field. It is essential to remember that the gases in the soil are quite as capable of translatory motion as the water. C. H. B.

Influence of the Composition of the Soil on the Physical Properties of Plants. By G. VILLE (*Compt. rend.*, **109**, 628—631).—The height of plants is in direct relation to the fertility of the soil. In the case of plants in which nitrogen-derivatives are the dominant constituents, a deficiency of nitrogen in the soil has a greater effect than a deficiency of any other constituent. In one and the same year, the same plant will attain to different heights in different soils, but variations due to a deficiency of fertilising agents are always in the same direction. The height at a given period of growth is practically the same in different years. The weight of similar crops varies from year to year, but the variations are always in the same direction for any given variations in the composition of the soil.

The proportion of carrotene in plants depends on the fertility of the soil, and increases with it. Variations in the proportion of chlorophyll follow the same order as variations in the proportion of carrotene.
C. H. B.

Production of so-called Sweet Fodder. By E. MACH (*Bied. Centr.*, **18**, 622—624, from *Tiroler landwirtsch. Blätter*, **8**, 137—139).—The object of the experiments was to determine whether the loss of food-substance in the preservation of green fodder by Fry's process is essentially smaller than in the preparation of sour fodder by the older methods. Two samples from a five months' old green maize silo were examined: the one was taken from the middle and was well preserved, the other from the edge, and badly preserved. They contained respectively 80·84 and 82·26 per cent. of water and volatile matter. The following table shows the percentage composition of the two samples (calculated on the dry substance), as well as the constituents of a sample of sweet maize, and the average composition of fresh, green maize (also on the dry substance):—

	Ensilage.		Sweet maize.	Average composition of fresh green maize.
	Good.	Bad.		
Nitrogenous substance	8·56	9·81	5·60	9·37
Crude fat	3·26	3·19	3·19	3·12
Non-nitrogenous extract	60·13	56·13	52·27	52·50
Crude fibre	33·31	30·65	28·34	30·00
Crude ash	15·00	12·48	7·76	—
Pure ash	10·00	8·71	4·91	6·25
Total free acid (as lactic acid)	—	—	2·00	—
Volatile acids (as acetic acid)	—	—	0·65	—
Dry substance	—	—	—	16·00

The fresh ensilage of good quality contained 0·320 per cent. (in fresh substance) of alcohol, 0·531 per cent. of free acid (calculated as lactic acid), 0·657 per cent. of volatile acids (as acetic acid), and 0·986 per cent. of total volatile acids (as acetic acid). The corresponding nnmbers for the bad sample are 0·280, 0·316, 0·356, and 0·535.

The sweet maize prepared by Fry's method does not differ essentially from the average composition of fresh maize. The sugar of the fresh maize has disappeared completely, whilst alcohol and free acids have been formed. The fact that a larger amount of volatile acid was found than total free acid is due to the liberation of volatile acids (originally present as salts) in the distillation of the substance in presence of tannic acid.

Analyses of the ensilage at a later period are also given. The whole of the free acid was found to consist of acetic and butyric acids; lactic acid was not present.
N. H. M.

Analytical Chemistry.

Estimation of Phosphorus in Phosphor-tin. By W. HEMPEL (*Ber.*, **22**, 2478).—Phosphor-tin is best analysed by Wöhler's chlorine method as employed in the analysis of Fahl-ore. The stannic chloride and phosphoric chloride which are formed are collected in concentrated nitric acid (about 10 c.c.); the vessel is washed out with dilute nitric acid (1 : 2), and the phosphoric acid is precipitated with ammonium molybdate and estimated directly.

F. S. K.

Recognition of Phosphoric Acid of Mineral Origin. By J. STOKLASA (*Chem. Centr.*, 1889, ii, 57, from *Listy. Chem.*, **13**, 153—154).—The author contends that the percentage of fluorine in bones as given by different authors is decidedly too high. Raw bones do not show any fluorine by the Lorenz reaction, whilst incinerated bones give only a slight indication of the presence of this element when tested in the same way. On the other hand, the author found the fossil bones of *Elephas primigenius* to contain 3·54 and 4·36 per cent. of ferric oxide and 2·08 and 2·98 per cent. of fluorine respectively in two different specimens. Bones found in the older alluvials on the island of Festigos contained 2·42 per cent. of ferric oxide, 1·58 of fluorine, 80·04 of tricalcium phosphate. Superphosphates prepared from this phosphate and also from bones were tested by the Lorenz reaction, with the result that fluorine was only found in the former, whilst of the several samples of the latter class of superphosphates only that from bone-ash gave any indication of fluorine, and then but slightly. On the other hand, remarks the author, Lorenz seems to have overlooked the fact that a series of mineral phosphates exist which contain but very little fluorine.

J. W. L.

Rapid Method of Estimating Arsenic. By E. POLENSKE (*Chem. Centr.*, 1889, ii, 58—59, from *Pharm. Zeit.*, **34**, 299—300). —The method consists in evolving the arsenic as hydrogen arsenide in a Marsh apparatus, deposition of the arsenic in a tube having three bulbs blown on it, and weighing first that part of the tube containing the "mirror," and secondly the tube after dissolving off the arsenic. The evolution flask is recommended to be of a capacity of 250 c.c., and to contain 80—100 grams of zinc. The apparatus includes an acid funnel 30 cm. long, having a U-formed bend, and the evolution flask is also connected with a washing flask containing lead nitrate solution, to which is attached a tube containing calcium chloride, and at the farther end, potash. The decomposing tube is attached to this. All air is expelled from the apparatus, first by adding 5 c.c. of concentrated sulphuric acid and 20 c.c. of water, and the reagents are at the same time tested for arsenic by heating the tube. The solution should not contain more than 4—5 milligrams of arsenic, and is allowed to drop into the acid funnel from a burette at the rate of 0·5—1·0 c.c. per minute. The gas escaping from the end of the

tube is passed through a solution of silver nitrate, and the evolution should not be too rapid for the bubbles to be counted. During the evolution of the hydrogen arsenide, two bunsen lamps are placed under the second and third bulbs: in order to test whether all the arsenic is evolved from the flask, the first is heated, and if a "mirror" forms it must be driven onwards into the second bulb, and after a time the same test may be applied again. When it is thus proved that arsenic no longer escapes from the flask, the tube is disconnected and reversed, and any arsenic which may have been deposited in the third bulb is driven into the narrow tube between the second and third bulbs. All the arsenic having been thus collected in this part of the tube, it is cut off and weighed, and after dissolving off the arsenic with nitric acid, it is weighed again, the difference giving the weight of arsenic. Metallic salts and organic substances interfere with the accuracy of the method. J. W. L.

Behaviour of Silicates when Fused with Phosphates. By K. HAUSHOFER (*Chem. Centr.*, 1889, ii, 53, from *Sitzungsber. der math.-naturw. Abt. bayr. Akad. Wiss.*, 1889, 8—11).—Many silicates, when fused to a bead with an alkaline phosphate in the blowpipe, swell up, evolve gases, and finally insoluble silica, either in the form of a skeleton or as flakes, is deposited. The evolution of gases is referred by the author to the presence of chlorine, sulphates, or water, and he draws attention to this part of the reaction as an aid in the recognition of the silicate under examination. For instance, hauyn and sodalite, owing to the evolution of the chlorine and sulphuric anhydride, may be distinguished from nepheline, which is but slowly attacked. In like manner, humite is distinguished from olivine by the evolution of hydrofluoric acid, and tourmaline and axinite from beryl. The micas of the scapolite group, epidote and vesuvian, lose their water of constitution, whereas the felspars, amphibole, and granites are but slowly attacked. Similar distinctions may be drawn between crystallised käumerite and the dense rhodochrome, and between pyrophyllite and agalmatolite. J. W. L.

Technical Analysis of Commercial Sodium Sulphide. By B. SHETLIK (*Chem. Centr.*, 1889, ii, 211, from *Listy. Chem.*, **12**, 205—206).—10 grams of the sulphide is dissolved in water, the solution diluted to $\frac{1}{2}$ litre, and 50 c.c. titrated with normal sulphuric acid, phenolphthaleïn being used as an indicator. If the titration is made in the cold, the quantity of acid required must be doubled, whereas if it is carried out at a boiling heat and the acid added until the red colour does not reappear on further boiling the solution, the acid used is equivalent to the sulphide. Insoluble sulphides which are decomposed by dilute acid may be titrated in this way. J. W. L.

Qualitative Analysis of the Ammonium Sulphide Precipitate. By F. MAYER (*Ber.*, **22**, 2627—2630).—The presence of chromium in this precipitate renders impracticable the separation by solution in hydrochloric acid and precipitation of the iron and aluminium by boiling with sodium acetate, since the chromium is sometimes wholly and sometimes partially precipitated, whilst if no

iron is present, it all remains in the filtrate. The author has found that the presence of excess of iron (at least 5 atoms to every atom of chromium) ensures the total precipitation of the chromium. He, therefore, recommends that where chromium is suspected and iron is not present in large quantities, ferric chloride should be added in excess before boiling with sodium acetate. L. T. T.

Analysis of Aluminium Sulphate. By F. BEILSTEIN and T. GROSSET (*Chem. Centr.*, 1889, ii, 60; from *Melanges, Phys. Chim. Bull., St. Pétersbourg*, **13**, 42—47).—The authors recommend the following method. 1—2 grams of substance is dissolved in 5 c.c. of water, 5 c.c. of a cold saturated solution of ammonium sulphate added, and the mixture well stirred during a quarter of an hour. 50 c.c. of 95 per cent. alcohol is added, and the precipitated ammonia alum filtered off and washed with 50 c.c. of alcohol. The filtrate contains all the free acid, which is determined by concentrating and titrating with decinormal alkali. The whole of the aluminium sulphate is precipitated as ammonia alum. J. W. L.

Estimation of Chromium and Copper in Iron and Steel. By C. REINHARDT (*Chem. Centr.*, 1889, ii, 60—61, from *Stahl u. Eisen* **9**, 404—405).—For the determination of chromium, 10 grams of borings or filings are dissolved with 100 c.c. hydrochloric acid in a covered beaker of 500 c.c. capacity, first without heat, then at a boiling heat, oxidised with potassium chlorate, concentrated to one half the volume, filtered into a $\frac{3}{4}$-litre Erlenmeyer flask, and the insoluble residue washed several times with dilute hydrochloric acid on the filter, and finally with water. The solution is now reduced at a boiling heat by the addition of 10—20 c.c. of sodium hypophosphite solution (200 grams in 400 c.c. of water), and afterwards the chromium is precipitated by the addition of zinc oxide in excess. The precipitate is dissolved in hydrochloric acid, a little more hypophosphite added, and the precipitation repeated. The chromium is separated from the zinc by precipitation with ammonia, which precipitation must be repeated. The chromic oxide, after ignition, is fused, together with the insoluble portion of the material, with 8 grams of a mixture of 4 parts of sodium chloride, 1 part of sodium carbonate, and 1 part of potassium chlorate. From the dissolved flux, the manganese is precipitated with alcohol, the silicic acid with hydrochloric acid and a little sulphurous acid, and the chromium finally precipated as oxide with ammonia. The copper is determined in 10 grams of the material: the hydrochloric acid solution is reduced with sodium hypophosphite, and the copper precipitated with hydrogen sulphide. J. W. L.

Volumetric Estimation of Chromium in Iron and Steel. By E. WAHLBERG (*Chem. Centr.*, 1889, ii, 194, from *Berg. u. Hüttenm. Zeit.*, **48**, 180—181).—0·5 gram of the metal is dissolved in boiling nitric acid, sp. gr. 1·20, evaporated to dryness, ground up, transferred to a platinum crucible, mixed with a mixture of 2 grams of magnesia, 1 gram of potassium chlorate, and 1 gram of sodium carbonate, and the whole heated, at first gently, then in the blast flame for one hour.

The mass is dissolved out with 50—100 c.c. of water, any small quantity of manganic acid reduced by a drop or two of alcohol, acidified with sulphuric acid, and the chromic acid estimated by adding a known quantity of ferrous sulphate and determining the amount unoxidised by titrating with potassium permanganate.

J. W. L.

Microscopical Test for Tantalum and Niobium. By K. HAUSHOFER (*Chem. Centr.*, 1889, ii, 62—63, from *Sitzungsber. der math.-naturw. Abt. bayr. Akad. Wiss.*, 1889, 3—8).—The substance to be tested is fused with a very small bead of sodium carbonate in the hottest part of the bunsen flame for 30—40 seconds. It is then treated on the object glass with one drop of water, and the form of the crystals left as the water evaporates is noted; if tantalic acid is present in excess, these are hexagonal plates, whereas an excess of niobic acid causes the formation of hexagonal prisms. If the residue is treated with hydrochloric acid, the columbite acids crystallise out. Addition of sodium hydroxide, slightly warm, causes the formation of hexagonal plates, consisting partly of stars and prisms. A simple test for the columbite acids consists in boiling 20 millgrams of the mineral with 0·8 c.c. of concentrated sulphuric acid, the solution being poured off from the insoluble part, diluted to 2—3 c.c., and a little zinc-dust added; the solution becomes sapphire-blue in a few minutes.

J. W. L.

Hardness of Water. By E. WALLER (*Analyst*, **14**, 108—112).—Attention is directed to the fact that in cases where, either from excessive hardness or from the presence of magnesium salts, it is necessary to dilute a water before applying the soap test, the results may vary widely according to the degree of dilution employed, especially if no deduction is made for the soap required to give a lather with pure water. The hardness of a mixture of calcium and magnesium solutions appears to be less than that of either of the individual solutions apart.

M. J. S.

Estimation of Chlorine in Water. By A. HAZEN (*Amer. Chem. J.*, **11**, 409—414).—An investigation of the ordinary method of estimating chlorine in water by titration with a silver solution, using potassium chromate as an indicator. It is found that an excess of silver is always required to make the colour reaction apparent; this excess is smaller the greater the amount of chromate used, provided that this does not colour the liquid so much as to obscure the end-point; it is also smaller when the volume of the liquid titrated is small. The amount of silver chloride precipitated also influences the result, and, other things being equal, the excess of silver solution used is nearly proportional to the amount of silver precipitated. To correct for this, the use of a silver solution 1 per cent. stronger than its normal value is recommended. It is still better to standardise the silver solution against a solution of sodium chloride; with such a solution, and making a correction for the volume of liquid titrated, accurate results were obtained. If the amount of chlorine is small, the water must be concentrated, a very little sodium carbonate being added to prevent loss of hydrochloric acid on boiling.

C. F. B.

Dynamical Theory of Albuminoïd Ammonia. By R. B. WARDER (*Amer. Chem. J.*, **11**, 365—378).—The integral calculus is applied to obtain formulæ representing the distillation of an aqueous solution of ammonia, and the conversion of albuminoïd matter into ammonia by alkaline permanganate. It is assumed that the "coefficient of volatility"—that is, the ratio of the concentration in any small portion of the distillate to that of the liquid in the retort—is constant. In the case of the formation of albuminoïd ammonia, the law of mass action is applied, and the particular formula is investigated which represents the reaction between one molecule each of three different substances (permanganate, potash, and a nitrogenous substance). Curves are given representing the formulæ obtained. It is found that the rate of formation of albuminoïd ammonia varies with the amounts of permanganate and of potash present, and also with the rate of distillation, and with the concentration of the original solution. The calculated ratios of the amounts of ammonia in successive portions of the distillate do not agree with those obtained by experiment; this discrepancy is attributed to the fact that there is not one simple reaction taking place, but several; and hence the curve actually obtained is the resultant of a number of curves.

It is also found that the amount of ammonia left in the retort when the distillation is stopped, as calculated from the formula, is much less than that actually left. This is attributed to the formation of intermediate compounds which only yield ammonia with great difficulty. The author finally concludes that Wanklyn's ammonia process gives valuable but purely comparative results, and is useless for the absolute estimation of organic nitrogen. C. F. B.

Estimation of Ferrocyanide in Gas-lime. By O. KNOBLAUCH (*Chem. Centr.*, 1889, ii, 211—212, from *J. Gasbeleucht. u. Wasserversorg*, **32**, 450—459).—10 grams of the well mixed and finely ground-up gas-lime is digested, with frequent agitation, for 15—16 hours with 50 c.c. of 10 per cent. potassium hydroxide in a flask graduated on the neck at 250 c.c. and at 255 c.c. The volume is then made up to 255 c.c., the whole well mixed, and filtered; 100 c.c. of the filtrate is added to a hot solution of ferric chloride (containing 60 grams of ferric chloride and 200 c.c. of hydrochloric acid in the litre), the precipitate collected and washed with hot water, the funnel being covered meanwhile. The filter-paper with the precipitate is again transferred to the beaker in which the precipitation took place, the precipitate treated with 20 c.c. of 10 per cent. potassium hydroxide, and the whole then transferred to a 250 c.c. flask and made up to that volume. 50 to 100 c.c. of the solution is filtered from the insoluble ferric hydrate and paper, 3—5 c.c. dilute sulphuric acid added, and the solution titrated with standard solution of cupric sulphate, which has been standardised with a solution of potassium ferrocyanide (4 grams in 1 litre). If hydrogen sulphide is present, it must be removed before the titration by adding 1—2 grams of lead carbonate. In applying this volumetric method for determining hydroferrocyanic acid with cupric sulphate, the indicator used is a drop of ferric chloride on a piece of filter-paper to which is applied a drop of the solution

under experiment; so long as an excess of potassium ferrocyanide is present, the formation of prussian-blue will at once take place. Towards the end of the titration it is necessary to filter very small quantities of the solution into a dilute solution of ferric chloride, when the last traces of soluble ferrocyanide can be observed.

J. W. L.

Absorption of Bromine by Fatty Acids. By G. HALPHEN (*J. Pharm.* [5], **20**, 247—249).—The process may be applied either to fats or to the fatty acids obtained from them; the results differ in the two cases, but are comparable amongst themselves. A saturated aqueous solution of bromine and one of sodium hydroxide coloured with eosin are required. 20 c.c. of soda-lye at 36° B. is added to 980 c.c. of water and 2 grams of eosin. 20 c.c. of carbon bisulphide and 10 c.c. of bromine solution of known strength are placed in a flask provided with a cork. The soda solution is run in gradually from a burette. After each addition, the flask is closed and shaken four or five times, and the addition repeated until the brown colour passes to a salmon tint. The bromine solution is titrated by means of the sodium solution before each estimation, as its strength varies constantly. 20 c.c. of carbon bisulphide is placed in a 250 c.c. flask, 1 gram of fatty acid is added, and an excess of bromine to the amount of about 0·5 gram. The flask is shaken up and allowed to remain for five hours; at the end of this time the absorption is complete. The excess of bromine is titrated by means of the soda solution; the brown mass formed gradually passes to a white, soapy solution which becomes rosy on the addition of a few drops of the soda solution in excess.

The vegetable oils absorb much more bromine than does lard, so that their presence in lard can thus be easily detected.—J. T.

Note.—The standard solutions could not be originated by the method given.

J. T.

Estimation of Citric Acid in Lemon Juice. By R. WILLIAMS (*Analyst*, **14**, 25—29).—The object of this paper is to recommend the use of sodium hydroxide with phenolphthaleïn as indicator for determining the acidity of lemon juice, instead of sodium carbonate with litmus-paper. Normal sodium citrate blues litmus-paper, but has no effect on phenolphthaleïn; accordingly titrations of pure citric acid made with sodium hydroxide and the latter indicator give numbers agreeing closely with theory, whilst those with the carbonate and litmus are low. Nevertheless, for some unexplained reason, the carbonate gives higher results than the hydroxide when applied to lemon juice, and estimations by precipitation as calcium salt agree better with the latter than with the former, being in fact generally lower than either.

M. J. S.

Impurities in Commercial Salicylic Acid. By B. FISCHER (*J. Pharm.* [5], **20**, 258—261; from *Pharm. Zeit.*, 1889, 329, after *Pharm. Zeit. Russ.*, 1889, **28**, 378).—Salicylic acid contains cresotic acid when manufactured from impure phenol containing cresol. The presence of potash in the sodium hydrate employed occasions the formation of parahydroxybenzoic acid; this acid is also produced if

the temperature is too low at the time when the current of carbonic anhydride is passed, whilst too high a temperature at this stage results in the production of hydroxyisophthalic acid, due to the action of the gas on the sodium salicylate already formed. Lastly, particularly in presence of iron salts, brown or yellow compounds are formed by oxidation, which are insoluble in water, and give a yellow colour to the salicylic acid. In a well-conducted process, parahydroxybenzoic and hydroxyisophthalic acids are usually not formed in quantities exceeding 0·4 per cent., and the first is easily removed by washing, as it is readily soluble in water. The second acid is less soluble in water, and may amount to 1 per cent. in certain cases. Cresotic acid is the most important impurity, as apart from its obscure physiological action, its presence is very objectionable. The amount of cresotic acid present may be estimated by titrating with decinormal baryta solution, using phenolphthaleïn as indicator. Owing to the difference in their molecular weights, less solution is required to saturate cresotic acid than is required by salicylic acid, but great care is needed to obtain satisfactory results, and certain accidental impurities should be previously sought for, namely, water, colouring matters, and sodium chloride. With this view, dissolve in ether; if the solution is not clear, filter, evaporate, and dry first at 60°, then in a vacuum over sulphuric acid. In the abseuce of these impurities, it is necessary to dry the sample. The baryta solution is standardised by the use of pure salicylic acid obtained by converting the commercial acid into the calcium salt, recrystallising, and then decomposing the salt by means of hydrochloric acid. For the detection of cresotic acid, 15 c.c. of water and 1 to 2 grams of calcium carbonate are boiled in a 200 c.c. flask; 3 grams of the salicylic acid is added, and the flask is agitated over a flame until the volume is reduced to about 5 c.c. By this time some crystals have formed. After cooling, the mother-liquor is transferred to a test tube and evaporated to 1 c.c. On rubbing this with a glass rod, crystallisation sets in. 1 c.c. of water is added, and the liquid filtered through a small plug of cotton. The filtrate is made up to 1 c.c. and hydrochloric acid is added; if the original acid contained 3 to 5 per cent. of cresotic acid, there separates out a mixture of acids which fuses in boiling water and collects at the bottom of the test tube in the form of thick, oily drops. The test does not succeed with less than 1 per cent. Hydroxyisophthalic acid may be separated from salicylic acid by distillation in a current of steam. The first acid remains in the still as a light-grey powder or as small lumps. By dissolving it in sufficient hydrochloric acid and filtering through charcoal, it can be obtained in the form of slender, white needles, which fuse with decomposition about 300—305°. The author has found in one sample of commercial salicylic acid 0·5 per cent. hydroxyisophthalic acid, and in another 5·5 per cent. of cresotic acid.

J. T.

Oil Testing. By F. Jean (*J. Pharm.* [5], **20**, 337—341).—The author's method comprises the determination of the density, melting point of the fatty acids, the elevation of temperature under the influence of sulphuric acid, and the refractive power. To determine the density, Wesphal's balance is employed. To determine the

melting point, a special apparatus is employed consisting of a thin U-shaped tube, in the two limbs of which are platinum wires nearly touching the bottom of the tube. A layer of solid acid comes between the ends of the wire, but this is displaced by mercury which has been charged in one side of the tube, when the temperature of a surrounding beaker of water has reached the melting point of the enclosed acid. The mercury causes electrical contact between the wires, and the transmitted current rings a bell when the temperature is read off, as given by a thermometer immersed in the bath. To determine the rise in temperature when mixed with sulphuric acid, a small beaker 4 cm. diameter and 6 cm. high is marked to contain 15 c.c., and in this is placed an acid tube provided with a stopper having a small tube through which air can be blown into the interior, and a small glass tube reaching from the bottom of the acid tube, and just passing through its side towards the upper end, so that on blowing into the acid tube its contents are expelled and mixed with oil in the beaker. 15 c.c. of the oil to be tested is placed in the beaker and heated to 40°, the acid tube is charged with 5 c.c. of sulphuric acid at 65° B. and placed within the beaker; the whole is allowed to cool down to 30°, and is then placed in a felt-lined box, when the acid is transferred to the oil by blowing and well mixed with it, the temperature is carefully observed, and the maximum reached is noted. In general, when this temperature and the density of the oil are satisfactory, the sample may be regarded as pure. Oils which have been oxidised or otherwise changed require treatment with alcohol, or, better still, saponification, before determining the rise in temperature. Sometimes when the rise of temperature is nearly the same for two oils, that of their two fatty acids may differ much more. One or two results may be given of oils and their acids:—Olive oil 41·5°, acid 45°; linseed oil 61°, acid 109°; colza (Pas-de-Calais) 37°, acid 44°; ditto (India) 37°, acid 46°. To determine the refractive power of the oil, a special oleorefractometer is employed which is not described. The index of refraction only varies within narrow limits for the same species if care be taken to remove excess of acid by treatment with alcohol. The purity of a sample may be safely affirmed when the index of refraction, the rise in temperature, and the density agree with a standard oil of known purity.

J. T.

Oil of Sesame. By W. Bishop (*J. Pharm.* [5], **20**, 244—247).— If this oil is shaken for a short time with pure hydrochloric acid of 21—22° B. in the proportion of 8 of oil to 12 of acid, no special effect is produced, but if the oil is exposed to air and solar light for some days, and the same test is applied, the mixture becomes green and, after a time, the colour is found to be confined to the acid layer. If the action of air and light be much prolonged, the green colour is intensified, and after a still longer period, a bluish-violet, flocculent precipitate is produced. The green acid solution gives an absorption-spectrum almost exactly coinciding with that of chlorophyll. The application of this reaction will serve to indicate, when the results are positive, that a sample of sesame oil has been

exposed to light and air for some time, and is not probably of recent production. Such an oil added to olive oil in the proportion of 5 to 10 per cent. can be easily detected by this method, whilst 10 to 20 per cent. of oil of sesame may be detected in the same way after some days' exposure. J. T.

Optical Examination of Oils and Fats. By E. H. AMAGAT and F. JEAN (*Compt. rend.*, **109**, 616—617).—Determination of the refractive index in a refractometer of special construction is a delicate and trustworthy means of detecting adulterations in oils and fats. The variations in the refractive indices of samples of the same oil from different sources are very slight, and distinctive differences are observed between vegetable oils, animal oils, and mineral oils. As little as 10 per cent. of oleomargarin can be detected in butter. C. H. B.

Analysis of Fats and Oils. By J. MUTER and L. DE KONINGH (*Analyst*, **14**, 61—65).—The authors' object has been to re-determine the iodine absorption (Hübl's) of the liquid fatty acids from various oils and fats under conditions which should be as uniform as possible, and should exclude any alteration of the acids either by exposure to air or by drying at a high temperature.

A weighed portion of the fat is saponified with alcoholic potash, and the solution accurately neutralised with acetic acid. It is then poured into an excess of a boiling solution of lead acetate. The precipitate is washed, then transferred to a stoppered bottle and treated with ether. The ether solution is filtered from lead stearate, &c., into a Mutër's "oleïn tube," in which it is decomposed by dilute hydrochloric acid. The volume of the ethereal solution of the fatty acids having been read, an aliquot part is run into a flask and most of the ether distilled off. The ether vapour protects the fatty acids from the air. Alcohol is then added, and the solution is titrated with soda; this gives the total amount of the liquid fatty acids, calculating them as oleic acid. Another portion of the ethereal solution containing 0·5 gram of the fatty acid is then evaporated in a bottle through which a stream of carbonic anhydride is being passed. When the last traces of ether are removed, 50 c.c. of Hübl's reagent is instantly added, and the bottle, having been stoppered, is placed in the dark for 12 hours, side by side with a blank, after which the excess of iodine is titrated by thiosulphate. The authors anticipate that the "iodine absorbing power" thus ascertained will permit the amount of any admixture of fats to be calculated with more precision than has hitherto been possible. M. J. S.

Extraction of Fat from Milk Solids. By H. D. RICHMOND (*Analyst*, **14**, 121—130).—Of the 15 or more methods which have been proposed for the extraction of the fat from the dry residue of milk, those of Adams (paper coil), Soxhlet (plaster of Paris), and Storch (pumice) give the highest and most concordant, but yet not identical results. The author has reinvestigated these three methods, using kieselguhr in place of pumice. In Adams' method, some analysts extract the paper coils with ether for a short time before

using them; others apply a correction based on blank experiments with the same batch of paper. The author finds that the complete extraction of the paper with ether requires a very prolonged treatment; the total extract in $7\frac{1}{2}$ hours being more than three times as much as that obtained in the first $1\frac{1}{2}$ hour. The matter extracted consists chiefly of the calcinm salt of a resinous acid. The most complete and rapid extraction is obtained by the use of alcohol containing 10 per cent. of acetic acid. After 3 or 4 hours' treatment with this reagent in a Soxhlet's apparatus, nothing soluble in ether remains. With the plaster and kieselguhr methods, the chief requisite is to grind the dried residue to a very fine powder, and to extract it with ether for at least 3 hours. Working in this way, the three methods agree closely. From the results of numerous determinations by the three methods, the author has developed a new formula for deducing the percentage of fat from that of total solids and the specific gravity: $T = 1{\cdot}17\ F - 0{\cdot}263\ \frac{G}{D}$ (apparently a misprint for $+\ 0{\cdot}263\ \frac{G}{D}$), where T is the percentage of total solids, F that of fat, D is the specific gravity of the milk, and $G = 1000\ (D - 1)$. This formula gives results which do not differ materially from those of Hehner and Richmond's older formula (*Analyst*, **13**, 32). The most satisfactory method of estimating the total solids appears to be the evaporation of not more than 2 grams of milk in a flat-bottomed basin and drying for 1 or $1\frac{1}{2}$ hour. M. J. S.

Volumetric Method for the Estimation of Fat in Milk, &c. By C. L. Parsons (*Analyst*, **14**, 181—187).—This method is proposed as one which can be carried out at the dairy by unskilled persons. 100 c.c. of the milk is placed in a bottle 11 inches high and $1\frac{1}{2}$ in diameter. 10 c.c. of soda solution (made by dissolving 1 part of commercial caustic soda in 2 parts of water) is added, then 5 c.c. of alcoholic soap solution (1 ounce of Castile soap to the gallon). 50 c.c. of gasoline (free from residue) is next added; the bottle is corked and shaken hard five or six times during half-an-hour. The petroleum solution of the fat is then allowed to rise to the surface. Should it fail to do so, 5 c.c. or more of the alcoholic soap solution may be added and gently mixed in. When the upper layer is perfectly clear, 25 c.c. of it is withdrawn and evaporated in a small flask, which has its neck cut off obliquely. Two drops of strong acetic acid is added to the fat, which is then dried at 120° for $1\frac{1}{2}$ hours and drained from the flask into a measuring tube graduated in twentieths of a cubic centimeter. A table given in the paper converts the readings of the volume of the fat into percentages. The necessary precautions are fully described.
M. J. S.

Condensed Milk and the Estimation of Caseïn and Lactalbumen. By H. Faber (*Analyst*, **14**, 141—147).—The author proposes to employ the estimation of the relative proportions of caseïn and lactalbumen as a means of distinguishing between fresh milk and that which has been condensed and afterwards diluted with water.

Fresh milk contains from 0·35 to 0·45, or perhaps more, of lactalbumen. By boiling the milk about two-thirds of this is coagulated, or so modified that it is precipitated together with the caseïn. The heating to about 75°, to which condensed milk must be subjected in order to sterilise it, has a similar effect. The two albuminoïds can be separated by Sebelien's method. The caseïn is first precipitated by magnesium sulphate, 2 vols. of the saturated solution of that salt being first added, and then as much of the powdered crystals as the mixture is able to dissolve; the precipitate is washed with a saturated solution of magnesium sulphate; and the lactalbumen is precipitated from the filtrate by either tannic acid or phosphotungstic acid. In these precipitates, the nitrogen is estimated by Kjeldahl's method. Test analyses show that the separation is very exact.

M. J. S.

Estimation of Soluble and Insoluble Fatty Acids in Butter. By W. JOHNSTONE (*Analyst*, **14**, 113—114) and H. D. RICHMOND (*ibid.*, 153—155).—Instead of estimating the volatile fatty acids by the Reichert process, the author prefers the following method. The butter is saponified with a known quantity of alcoholic potash and the excess found by titration. The alcohol having been removed by boiling, an excess of acid is added, and the insoluble fatty acids are filtered off and washed. After air-drying they are dissolved by ether and weighed after evaporation. They are now again saponified by standard potash, and the amount they neutralise is ascertained. The difference between these two titrations gives the amount of fatty acid soluble in water, which thus estimated is considerably higher than is shown by Reichert's process. The author hints that the results of the latter may be vitiated by the production of propionic, acetic, and formic acids by the action of potash on the glycerol. Richmond, commenting on the above process, shows that the results given cannot possibly be correct, the total fatty acids, together with the glycerol residue corresponding to the potash neutralised, adding up to more than the weight of the butter taken, and that this is due to the titration of the insoluble acids being performed in aqueous solution. The results by Reichert's process, when corrected for the recognised average deficiency of $\frac{1}{10}$, add up almost exactly to 100 per cent. He points out that at the temperature of the water-bath potash has no action on glycerol.

M. J. S.

Examination of Lard for Adulteration. By T. S. GLADDING (*Analyst*, **14**, 32—34).—The following tests should all be applied to a suspected sample:—(1) specific gravity at 100°; (2) Hübl's iodine test; (3) Bechi-Millian test (Abstr., 1889, 319); (4) Dalican's "Titre" test; (5) Belden's microscopic test for beef fat (*Analyst*, **13**, 70). Dalican's "titre" is the temperature of crystallisation of the fatty acids. These are to be prepared from the sample by saponification, washed well with hot water, and filtered through dry paper into a test-tube. The crystallising point is then taken with a thermometer graduated to tenths of a degree. The titre of lard may range from 36·4° to 41·4°; iodine absorption from 57 to 68·4 per cent., a high titre being associated with a low iodine absorption, and *vice versâ*.

The titre of beef fat is about 41·6 to 44; iodine absorption, 43·8 to 40; that of cotton-seed oil, 33·3, iodine absorption, 108. The one adulterant will therefore to some extent mask the other; they are, however, respectively revealed by Bechi's and Belden's tests. The high specific gravity of cotton-seed oil affords the only means of estimating the amount of it present. (See also Abstr., 1889, 319, 659.)

M. J. S.

Action of Acids on Benzoic Sulphinide and Analysis of "Saccharin." By I. REMSEN and W. M. BURTON (*Amer. Chem. J.*, 11, 403—408).—When benzoic sulphinide, $C_6H_4<{CO \atop SO_2}>NH$ [= 1 : 2], is boiled with dilute acids, hydrogen ammonium orthosulphobenzoate, $COOH\cdot C_6H_4\cdot SO_3NH_4$ [= 1 : 2] is formed, together with a little orthosulphaminebenzoic acid, $COOH\cdot C_6H_4\cdot SO_2NH_2$. The best strength of acid is that obtained by diluting strong hydrochloric acid of sp. gr. 1·17 with 8 to 10 times its volume of water.

Commercial "saccharin" is found to be a mixture of parasulphaminebenzoic acid, benzoic sulphinide. and hydrogen potassium orthosulphobenzoate, the amount of sulphinide present being somewhat less than 50 per cent.

To analyse it, 2 grams are boiled for one hour with 100 c.c. of dilute hydrochloric acid (1—8) in a flask of 250 c.c. capacity, provided with a reflux condenser. The clear solution is then evaporated to about 15 c.c., when the parasulphaminebenzoic acid separates out; it is dried at 80° and weighed. The filtrate, containing hydrogen ammonium orthosulphobenzoate (from the decomposition of the sulphinide) and the hydrogen potassium salt of the same acid, is evaporated; the residue is weighed, and the amount of potassium in it is estimated by heating a portion with sulphuric acid, and weighing the potassium sulphate formed. Two samples of saccharin were analysed, each five times; the mean percentage composition of each is given below.

	$COOH\cdot C_6H_4\cdot SO_2NH_2$.	Benzoic sulphinide.	$COOH\cdot C_6H_4\cdot SO_3K$.
I	50·00	42·86	7·12
II	44·49	48·33	7·99

C. F. B.

Estimation of Morphine in Opium. By F. A. FLÜCKIGER (*Arch. Pharm.* [3], **27**, 721—732, 749—772).—The author discusses various points which arise in the estimation of morphine, and arrives at the following fairly good, although not quite perfect, method. 8 grams of opium powder is placed in a folded filter of 12 cm. diameter with a little tapping, and is dried at 100°. After half an hour 10 c.c. of ether mixed with 10 c.c. of chloroform is poured over it, the covered funnel being frequently struck, and finally 10 c.c. more of chloroform is poured on. After all possible liquid has run through, the filter with its contents is opened out and dried at a gentle heat. Next the powder is vigorously and repeatedly shaken in a flask with 80 c.c. of water and filtered after two hours. 42·5 grams of the filtrate is well and often shaken in a weighed flask with 7·5 c.c.

of alcohol (0·83 sp. gr.), 15 c.c. of ether, and 1 c.c. of ammonia (0·96). After six hours, the contents of the flask are poured on to a double-folded filter of 10 cm. diameter, and the morphine is washed on to the filter with about 10 c.c. of water. This is dried, returned to the dried flask, and dried at 100° until its weight becomes constant. This process with a particular sample gave 12·90, 13·12, 13·35 per cent. of morphine, which was not pure white, but which dissolved completely in lime-water with very little colour. As an appendix the author criticises in some detail an article by E. R. Squibb in the "Ephemeris" for July, on morphine estimation, and, although he sees many defects in the process given, he remarks that the comprehensive paper deserves the fullest consideration. J. T.

Analysis of Pepper and the occurrence of Piperidine in the same. By W. Johnstone (*Analyst*, **14**, 41—49).—Moisture and ash.—A weighed portion is dried at 100° and then incinerated in a muffle. The ash is treated successively with water and hydrochloric acid, and the amount of insoluble matter noted.

Oil.—20 grams is distilled with water; the distillate is shaken with ether, the ethereal solution is evaporated at a very low temperature, and the residue is dried over sulphuric acid.

Piperidine.—20 grams is distilled as for the oil determination, and the distillate is titrated with N/10 sulphuric acid (compare Abstr., 1889, 298). That the piperidine is not derived from the hydrolysis of piperine is shown by the fact that pure piperine yields no piperidine when distilled with water, also that in distilling pepper with water, piperidine soon ceases to come over, although the amount obtained is very small in comparison with the piperine present.

Piperine.—10 grams is digested at 100° in a closed bottle with 3 grams of potash dissolved in 25 c.c. of water and 25 c.c. of alcohol. The bottle (4 oz.) should have the neck ground flat and be closed by a plate of caoutchouc pressed tightly upon it by a screw-frame. After 4—6 hours' digestion, the bottle is cooled, the contents are washed into a large flask and distilled as long as the distillate is alkaline. The theoretical yield of piperidine is obtained.

Crude Fibre.—A small quantity is boiled for half an hour in a flask with inverted condenser with 200 c.c. of dilute sulphuric acid (12·5 grams per litre). The residue is twice boiled with water, then with 200 c.c. of potash (12·5 grams per litre), and again twice with water. It is collected on a tared filter, dried and weighed, and any ash it contains deducted.

Nitrogen.—Determined by soda-lime, as usual.

Alcoholic Extract.—10 grams is extracted with 95 per cent. alcohol in a Soxhlet's apparatus for 24 hours. The alcohol is distilled off and the extractive matters dried at 100°.

Starch.—The exhausted residue from the preceding is, without drying, washed into a flask with 200 c.c. of water and 20 c.c. of hydrochloric acid (1·121) and heated in boiling water for three hours. After cooling, the liquid is filtered, neutralised with soda, made up to 500 c.c., and titrated with Fehling's solution.

In 13 genuine samples from various localities, the moisture ranged

from 12 to 15 per cent., ash 1·07 to 4·46 (long pepper 7·57), oil 0·53 to 1·87, piperidine 0·21 to 0·77, piperine 5·21 to 13·03, fibre 4·2 to 15·05, starch 29·6 to 53·5, ash insoluble in acid 0·06 to 0·62 (long pepper 1·47). Any larger amount of insoluble ash would probably be the best indication of a fraudulent addition. M. J. S.

Detection of Cocaïne Hydrochloride. By M. GOELDNER (*Arch. Pharm.* [3], **27**, 799; from *Pharm. Zeit.*, **34**, 471).—The author believes that the following is a characteristic test for cocaïne. 6 or 7 drops of pure, strong sulphuric acid are added to some crystals of resorcinol in a porcelain basin, and the latter is moved to and fro a little, then a little cocaïne hydrochloride is added to the yellow liquid. A somewhat strong reaction follows, and a splendid, blue coloration is immediately obtained; a drop of sodium hydroxide changes this to a light-rose colour. The reaction goes more quickly with powdered resorcinol in place of crystals. Very small quantities of the reagent give no colour reaction. Other alkaloïds give nothing approaching to this reaction. J. T.

Estimation of Indigotin for Commercial Purposes. By F. A. OWEN (*Chem. Centr.*, 1889, ii, 217—218; from *J. Amer. Chem. Soc.*, **10**, 178).—1 gram of the substance is weighed on a watch-glass, dried at 100°, finely powdered, rubbed with water to a thin paste, and washed into a 250 c.c. flask. 3 grams of zinc-dust and 6 grams of sodium hydroxide are added, the solution diluted to a little above the mark, shaken up now and then, and after the reaction is complete (during which the solution must remain green, red or brownish streaks indicate that the reduction has been carried too far; a froth indicates the presence of too much zinc), 50 c.c. of the clear liquid is exposed to the air for half an hour, acidified with hydrochloric acid, and filtered through a well-washed filter, dried at 100°, and weighed. J. W. L.

General and Physical Chemistry.

Emission Spectrum of Ammonia. By G. MAGNANINI (*Zeit. physikal. Chem.*, **4**, 435—440).—The author has determined the positions of a large number of the lines of the ammonia spectrum. These are compared with the lines of Hasselberg's second hydrogen spectrum, with which they show a remarkable coincidence. H. C.

Absorption Spectrum of Nitrosyl Chloride. By G. MAGNANINI (*Zeit. physikal. Chem.*, **4**, 427—428).—The absorption spectrum of nitrosyl chloride vapour consists of six absorption bands in the orange and green parts of the spectrum. The wave-lengths corresponding with these bands and their relative intensities are given. H. C.

Electromotive Force of Selenium. By S. KALISCHER (*Ann. Phys. Chem.* [2], **37**, 528).—The author observes that Righi (Abstr., 1889, 555) appears to have misunderstood a remark made by him in a former note (*ibid.*, 3). He had pointed out that selenium cells often give an E.M.F. before exposure to light, and that, therefore, before experimenting on the influence of light on them, they should be tested in the dark to see if they already give any E.M.F. He had no intention of asserting the necessity of actually manufacturing the cells in darkness, and preventing their even being exposed to light before experimenting with them. G. W. T.

Electrical Conductivity of Hydrogen Chloride in Different Solvents. By I. KABLUKOFF (*Zeit. physikal. Chem.*, **4**, 429—434).—The conductivity of solutions of hydrogen chloride in benzene, xylene, hexane, and ether is excessively small, that in ether being greatest and that in benzene the least. The molecular conductivity of the solution in ether is found to decrease with rising dilution. Solntions of hydrogen chloride in methyl, ethyl, isobutyl, and isoamyl alcohols have a somewhat greater conductivity. The methyl alcohol solutions have the highest conductivity, being about four times greater than the ethyl and 30 times greater than the isobutyl alcohol solutions. Amyl alcohol, like ether, gives a decreasing molecular conductivity with rising dilution. Hydrogen chloride was also examined in aqueous solutions of ethyl alcohol. The presence of ethyl alcohol is found to greatly decrease the conductivity of hydrogen chloride in water, an addition of 6 per cent. of alcohol causing a decrease of 20 per cent. in the conductivity.

If a solution of benzene saturated with hydrogen chloride is allowed to remain for two or three days, crystals separate out which melt without decomposition, and can be sublimed at high temperature. They are probably of the composition $C_6H_6,3HCl$. H. C.

Electrical Conductivity of Solid Mercury. By L. GRUNMACH (*Ann. Phys. Chem.* [2], **37**, 508—515).—As the result of a further experimental investigation of this subject, the author finds that the apparent resistance of mercury when just melted is 2·5 times its value just before liquefaction begins.

The value 1·5 formerly obtained by the author (Abstr., 1889, 201) is, therefore, too small. The value now obtained by him is smaller than that given by Cailletet and Bouty, namely 0·4, and the author attributes the difference between his present and former results, and between both of them and that obtained by Cailletet and Bouty, in great part to the change in volume which mercury undergoes in passing from the solid to the liquid state, and the effects of this change of volume on the resistance, depending as they do on the dimensions of the tubes and their regularity of bore. The degree to which the result is affected in this manner cannot be determined until these changes of volume have been measured, and the author states that an investigation of this point has been commenced.

The results of the investigation described in this paper confirm the conclusion formerly arrived at by the author, that the temperature-coefficient of decrease of resistance for solid mercury decreases from the solidifying point down to −80°, the lowest temperature at which observations were made.

The values obtained for this coefficient in the former and present series of observations respectively are given below:—

Range of temperature.	Temperature-coefficient. First series.	Temperature-coefficient. Second series.
−80° to −70°	0·0010	0·0008
−70 „ −60	0·0010	0·0011
−60 „ −50	0·0012	0·0013
−50 „ −40	0·0017	0·0023

The results of the present investigation therefore confirm the conclusion formerly arrived at by the author, that assuming the truth of Clausius's law expressing the relation between the electrical resistances of simple metals and their absolute temperatures, then mercury must be considered as an exception. G. W. T.

Thermoelectric Currents between Amalgamated Zinc and Zinc Sulphate. By K. A. BRANDER (*Ann. Phys. Chem.* [2], **37**, 457—462).—The primary object of the investigation was to determine the relation between the E.M.F. developed and the difference of temperature between the electrodes.

The electrodes, of amalgamated zinc, were placed in two vessels communicating by means of a siphon, and filled with a solution of zinc sulphate. One of these vessels was kept at the temperature of the place of observation, while the temperature of the other was gradually raised.

The author found that, within the limits of errors of observation, the E.M.F. was proportional to the difference of temperature, until this

difference exceeded 20·45°, after which the E.M.F. appeared to increase rather more rapidly than the temperature difference. A few experiments were also made to determine the effect of varying the concentration of the zinc sulphate solution, and their results showed that the E.M.F. increased with the concentration. G. W. T.

Electrochemistry and Thermochemistry of some Organic Acids. By H. Jahn (*Ann. Phys. Chem.* [2], **37**, 408—443).

Formic Acid.—When a solution of sodium formate in water was acidified with formic acid and subjected to electrolysis, it yielded hydrogen and carbonic anhydride. The sodium salt must first be resolved into sodium and the group HCO_2, the former forming sodium hydroxide with the water of solution, whilst the latter must either break up into carbonic anhydride and hydrogen or form formic acid again with the water of solution, according to the equation $2H + CO_2 + H_2O = 2H_2CO_2 + O$, the free oxygen then combining with a portion of the formic acid to form carbonic anhydride and water. Now Bunge has shown that in the electrolysis of formic acid no hydrogen is given off at the anode, which excludes the first explanation, and shows that a simple combustion of the acid takes plaee at the anode. The results were confirmed by determinations of the amount of gas liberated by the passage of a measured quantity of electricity.

The author made a series of determinations of the heat of combustion of formic acid which agreed very well together, and their mean gave 62·87 cal. as the heat of combustion of a milligram molecule of formic acid. Thomsen obtained the value 60·2 cal., and the author observes that this may be considered as a very close agreement, considering that, as Ostwald has shown, the heat of combustion varies considerably with the temperature.

Acetic Acid.—A solution of sodium acetate in water was electrolysed at the temperature 0°. A considerable quantity of carbonic anhydride was formed, and after the gas given off had been freed from this, the residue was found to consist of hydrogen and ethane, about 65 per cent. of the former and 35 per eent. of the latter. Very slight traces of iodoform were obtained from the liquid residue in the electrolytic cell. From this it follows that the action consisted in the setting free of acetic acid at the anode, and its combination with the oxygen simultaneously liberated; but if this took place entirely in the manner usually assumed, $2C_2H_4O_2 = C_2H_6 + 2CO_2 + H_2O$, the volumes of hydrogen and of ethane would have been equal. The excess of hydrogen present, combined with the absence of free oxygen, shows that part of the aeetic acid must have been burnt to form carbonic anhydride and water, according to the equation $C_2H_4O_2 + O_4 = 2CO_2 + 2H_2O$. In some quantitative experiments made with stronger currents, the proportion of hydrogen was found to be somewhat smaller. The proportion of hydrogen present in the evolved gases was also found to diminish as the strength of the solution was increased. These results show that the complete combustion of the acetic acid to carbonic anhydride and water is favoured

by increasing the strength of the decomposing current, and by diminishing the strength of the solution.

Assuming Thomsen's values for the heats of solution required for the calculation, the author determined the heat of combustion of the milligram molecule of liquid acetic acid to water and gaseous carbonic anhydride to be 208·81 cal., which is in very fair agreement with the values 210·3 obtained by Fabre and Silbermann, and 210·79 obtained by Stohmann. It follows from the last result that the heat absorbed in the formation of one milligram molecule of liquid acetic acid from amorphous carbon and water vapour is 121·61 cal.

Propionic Acid.—The results obtained with acetic acid suggested that propionic acid would probably be resolved into normal butane and carbonic anhydride, and the electrolysis of a solution of sodium propionate in water, acidified with propionic acid, showed that this reaction did actually occur, but it was veiled to a considerable extent by the decomposition of part of the acid into ethylene and carbonic anhydride, evidently according to the equation $C_2H_6O_2 + O = C_2H_4 + CO_2 + H_2O$. The author considers that the results of his experiments with acetic and propionic acids point to the conclusion that the ethane and butane formed during electrolysis are the results of the decomposition of double molecules, which exist in concentrated solutions, but are broken up into simple molecules when the solutions are diluted.

Oxalic Acid.—The electrolysis of an aqueous solution of potassium oxalate at the temperature 0° gave a gas consisting only of carbonic anhydride and hydrogen, so that the oxalic acid set free at the anode must have been completely burned to carbonic anhydride and water, according to the equation $H_2C_2O_4 + O = 2CO_2 + H_2O$. The heat of combustion of oxalic acid per milligram molecule was found to be 74·49 cal. G. W. T.

Thermochemistry of Methyl Alcohol and Solid Methyl Salts. By F. STOHMANN, C. KLEBER, and H. LANGBEIN (*J. p. Chem.* [2], **40**, 341—364).—The authors give details of the determination of the following thermal values (see table, p. 101). The figures in the sixth column represent the excess or deficiency of the heat of combustion of the methyl salt when compared with the sum of the heats of combustion of the acid from which it is formed and methyl alcohol (compare Berthelot, *Mécanique Chimique*, **1**, 407).

The authors then point out the difference between the heats of combustion of the various isomerides in this table, and also give a table showing the value of the affinity constant K (Ostwald, Abstr., 1889, 818) for 24 acids, 20 of which agree with the rule.

Table of thermochemical results with methyl-compounds.

Substance.	Formula.	Molecular weight.	Heat of combustion.	Heat of formation.*	
			Cal.	Cal.	
Methyl parahydroxybenzoate	$C_8H_8O_3$	152	896·0	132·0	+0·5
Methyl anisate	$C_9H_{10}O_3$	166	1069·3	121·7	−3·5
Methyl cinnamate	$C_{10}H_{10}O_2$	162	1213·6	71·4	−0·7
Methyl gallate	$C_8H_8O_5$	184	801·3	226·7	+3·4
Methyl β-naphthoate	$C_{12}H_{10}O_2$	186	1402·4	70·6	−3·4
Dimethyl phthalate (liquid)	$C_{10}H_{10}O_4$	194	1120·4	164·6	—
Dimethyl phthalate (solid)	$C_{10}H_{10}O_4$	194	1113·9	171·1	−1·1
Dimethyl isophthalate	$C_{10}H_{10}O_4$	194	1117·7	173·3	−1·7
Dimethyl terephthalate	$C_{10}H_{10}O_4$	194	1112·2	172·8	−0·1
Dimethyl oxalate	$C_4H_6O_4$	118	402·1	180·9	−0·7
Dimethyl succinate (solid)	$C_6H_{10}O_4$	146	703·6	205·4	−5·6
,, ,, (liquid)	$C_6H_{10}O_4$	146	708·5	200·5	—
Dimethyl fumarate	$C_6H_8O_4$	144	664·7	175·3	−3·4
Trimethyl trimesate	$C_{12}H_{12}O_6$	252	1292·5	249·5	−13·1
,, citrate	$C_9H_{14}O_7$	234	983·5	345·5	+2·9
Hexamethyl mellitate	$C_{18}H_{18}O_{12}$	426	1825·6	487·4	−13·8
Citric acid	$C_6H_8O_7$	192	474·6	365·4	—
Methyl alcohol	CH_4O	32	170·6	61·4	—

* C = 94 Cals.; H_2 = 69 Cals.

A. G. B.

Thermochemistry of Nicotine. By A. COLSON (*Compt. rend.*, **109**, 743—745).—*Nicotine*.—Heat of dissolution +6·6 Cals. at about 15°; heat of neutralisation by hydrochloric acid, 1st equivalent = 8·05 Cals.; 2nd equivalent = 3·47 Cals. Total heat of neutralisation by 4 mols. HCl = 12·06 Cals. With sulphuric acid, 1st equivalent = 9·54 Cals.; total heat of neutralisation by excess of acid = 13·46 Cals. It is evident that the two basic functions of nicotine have very different energies, a fact which is also shown by colour reagents. With litmus as indicator, nicotine has only one basic function, but with dimethyl-orange it has two.

The author has also made the following determinations:—

	Pyridine. Cals.	Piperidine. Cals.
Heat of dissolution	2·25	6·50
Heat of neutralisation, 1 mol. HCl	5·20	13·01
,, ,, 1·5 mol. HCl	5·20	—
,, ,, 1 mol. H_2SO_4	—	13·68

C. H. B.

Apparatus for making Vapour-density Determinations under Reduced Pressure. By J. F. EYKMAN (*Ber.*, **22**, 2754—2758).—The author describes with the aid of diagrams an apparatus in which vapour-density determinations may be made under reduced pressure, and in an atmosphere of hydrogen or some other indifferent gas.

The apparatus consists of a bulb-tube (A), somewhat similar in

shape to that employed in V. Meyer's method; this is heated by some suitable vapour in the ordinary way. A weighed quantity of the liquid, the vapour-density of which is to be determined, is placed in a small, sealed, pipette-shaped tube, and suspended in a chamber in the upper extremity of the bulb-tube (A). The latter is connected at the top with a graduated manometer tube, placed perpendicularly and open below, and also with a 3-way cock, so that it can be exhausted and filled with hydrogen or any other gas. The apparatus having been completely filled with hydrogen, it is exhausted as completely as possible, the open end of the manometer being immersed in mercury; the bulb-tube is then heated at a constant temperature, and hydrogen is allowed to enter until the required pressure is obtained. As soon as no more mercury flows out of the manometer tube, the pressure is noted on the scale, and the neck of the bulb containing the substance is broken without opening the apparatus, by an ingenious device, so that it drops to the bottom of the bulb-tube (A), and is there converted into vapour. The pressure is thereby increased, and the mercury which flows from the manometer tube is collected in a tared vessel; the increase of pressure is ascertained either by weighing the mercury, the diameter of the manometer tube having been previously determined, or from the difference in the readings on the manometer scale. The vapour-density is calculated from the increase of pressure produced by the vaporisation of a known weight of the substance in a vessel of known volume under known conditions of temperature and pressure.

Experiments with safrole (b. p. 232°), ethyl cinnamate (b. p. 271°), naphthylamine (b. p. 300°), phenylpropionic acid (b. p. 200°), and other substances gave very satisfactory results.

The apparatus can be employed also for making determinations by V. Meyer's method in the usual way. F. S. K.

Specific Volumes of some Ethereal Salts of the Oxalic Acid Series. By A. Wiens (*Annalen*, **253**, 289—318; compare W. Lossen, Abstr., 1888, 335).—A comparison of the molecular volumes of metameric ethereal salts of oxalic, malonic, succinic, and glutaric acids, containing normal alkyl radicles, shows that the larger the quantity of carbon in the acid radicle the smaller the molecular volume at 0°. This is generally the case at the boiling point also, but two exceptions were noticed, the molecular volume of ethyl propyl malonate being smaller than that of ethyl succinate, and that of butyl malonate smaller than that of propyl butyl succinate; these exceptions may be due to the uncertainty of the determinations at the boiling point.

The difference in molecular volume corresponding with the difference in composition increases in homologous series with the quantity of carbon in the compound. The difference between the molecular volume of ethyl methyl succinate and ethyl butyl succinate, for example, is 71·3; that between ethyl butyl succinate and ethyl heptyl succinate, 76·4. The same has been found to hold good for ethereal salts of monobasic acids, ethers, phenol ethers, and alkyl iodides.

A comparison of the molecular volumes at 0° shows that an increase by the group CH_2 in the empirical formula corresponds with various

differences in molecular volume, according to the manner in which this increase takes place. The increase in molecular volume by the conversion of the group C_nH_{2n+1} into $(CH_2)_x{\cdot}C_nH_{2n+1}$ (excluding methyl salts) is, on the average, 16·8 for each CH_2 group, but the difference between the ethyl and methyl salts is, on the average, 18·1. The increase, due to the conversion of the group CH_2 into $(CH_2)_n$, is, on the average, 16 for each additional CH_2 group, but when the group CH_2 is converted into CHMe (ethyl into isopropyl, for example), the corresponding increase in molecular volume is, on the average, 17·7.

The numerous experimental determinations are given in tables.

F. S. K.

Absorption of Gases by Mixtures of Alcohol and Water. By O. LUBARSCH (*Ann. Phys. Chem.* [2], **37**, 524—525).—The author observes that the publication of Müller's determinations of the absorption of carbonic anhydride by mixtures of alcohol and water (Abstr., 1889, 816) has induced him to publish the results obtained so far in an investigation of the absorption of various gases by mixtures of alcohol and water; these are given in the accompanyiug table, showing the percentages by volume of the gases absorbed at 20° and 760 mm. pressure by solutions containing the various percentages of alcohol (by weight) given in the first horizontal line:—

Percentage of alcohol....	0·00	9·09	16·67	23·08	28·57	33·33	50·00	66·67	80·00
Oxygen	2·98	2·78	2·63	2·52	2·49	2·67	3·50	4·95	5·66
Hydrogen ...	1·93	1·43	1·29	1·17	1·04	1·17	2·02	2·55	—
Carbonic oxide	2·41	1·87	1·75	1·68	1·50	1·94	3·20	—	—

The table shows that the minimum absorption for all three gases occurs at about the same proportion of alcohol to water, and this is the same as that found by Müller for carbonic anhydride, and therefore it seems probable that other gases will be found to behave in the same way.

G. W. T.

Simultaneous Solubility of Sodium and Potassium Chlorides. By A. ÉTARD (*Compt. rend.*, **109**, 740—743).—The sum of the salts dissolved between −20° and +180° is represented by a straight line, $y_{-20}^{+180} = 27{\cdot}0 + 0{\cdot}0962t$. Calculating from this coefficient the temperature at the *limit of solubility*, that is, the point at which, by reason of the increase in the proportion of salt and the decrease in the proportion of water, the latter has disappeared, the temperature obtained is 738°, which, according to Carnelly, is the melting point of potassium chloride.

In presence of potassium chloride, the curve of solubility of sodium chloride between −20° and +75° is parallel with the axis of temperature. Beyond 75° it decreases, and at 97° becomes identical with that of potassium chloride, after which it decreases to 120°, and then becomes constant (16·7 per cent.).

The solubility of potassium chloride alone is represented between

$-10°$ and $+75°$ by a right line with a coefficient 0·1470, and between 75° and 180° by a second right line, which has a coefficient of 0·0793, and a limiting point at 913°, or considerably above the melting point of the salt.

In presence of sodium chloride, the curve of solubility of potassium chloride between $-20°$ and $+75°$ is a right line $y = 10·3 + 0·0962t$; from 75° to 120° the solubility increases rapidly, and above 120° it is represented by a right line with the same coefficient as between $-20°$ and $+75°$. Its limiting point is 913°, and hence the curves of solubility of potassium chloride alone and in presence of sodium chloride are not parallel, but converge to 913°.

At the limiting point for the mixed salts, 738°, the proportion of the two salts would be 16·7 per cent. of sodium chloride and 83·3 per cent. of potassium chloride. The total quantity of chlorine is practically equal to the sum of the metals.

The curve representing the quantity of chlorine in solution is a right line; that representing the sum of the salts is also a right line; and hence the sum of the metals is likewise represented by a right line. The curve of the chlorine and the curve of the sum of the metals intersect at 738°. C. H. B.

Determination of Molecular Weights of Substances from the Boiling Points of their Solutions. By H. W. WILEY (*Chem. News*, **60**, 189—190).—"The apparatus employed consisted of an oval-round bottom flask of about 200 c.c. capacity," with a side tube from the neck connected with a condenser to keep volume of liquid constant. A thermometer graduated to tenths, but capable of being read to 0·02 of a degree was employed, the bulb being enveloped in fine copper foil to prevent interference of bubbles of steam. Sodium chloride was used to determine the factor, the number obtained, 8·968, was used for calculating the results in the following table; the volume of water being in all cases 150 c.c.; the temperature of boiling water was 99·50° except during the experiments with sodium nitrate, when it was 99·44°.

Substance taken.	Wt. taken in grams.	Total rise of temperature.	Molecular weight.	
			Calculated.	Theoretical.
KCl	6·0	0·35°	76·91	74·5
KBr	6·0	0·29	123·7	119·0
KI	9·0	0·33	163·1	166·0
KNO_3	6·0	0·33	108·7	101·0
$K_2Cr_2O_7$	18·0	0·38	283·2	295·0
$NaNO_3$	6·0	0·42	85·4	85·0
Saccharose	20·0	0·20	643·2	342·0
Oxalic acid	6·0	0·20	179·4	90·0

It will be noticed that the two organic compounds give double the theoretical molecular weight by this method. The results

obtained with salts containing water of crystallisation do not agree with the molecular weights with or without this water. These results were obtained quite independently of those of Beckman.

D. A. L.

Behaviour of Colloïd Substances with Respect to Raoult's Law. By E. PATERNO (*Zeit. physikal. Chem.*, **4**, 457—461).—The reduction of the freezing point by colloïd substances in water is very slight, and therefore leads to very high numbers for the molecular weights of such substances (Brown and Morris, Trans., 1889, 462). This, the author has observed, is the case with gallic and tannic acids; which behave like colloïds in aqueous solution and give molecular weights many times greater than those ordinarily accepted for these substances. If, however, solutions in acetic acid are taken, the behaviour is found to be perfectly normal, and the reduction of the freezing point is that corresponding with the ordinary simple molecular weights. Hence substances only behave as colloïds towards certain solvents, and the author holds that when a solid dissolves as a colloïd, the laws of freezing are not applicable to its solutions.

H. C.

Can Raoult's Method distinguish between Atomic and Molecular Union? By R. ANSCHÜTZ (*Annalen*, **253**, 343—347; compare Anschütz and Pulfrich, Abstr., 1888, 1273).—The depression produced by naphthalene picrate in the freezing point of benzene corresponds with that which would be produced by its constituent parts present together in an uncombined state. The author concludes therefore that the combination of the components of naphthalene picrate and analogous substances such as dimethyl diacetylracemate is not dependent on atomic union in the sense of the valence theory, but on molecular union.

If Raoult's method is capable of deciding between atomic and molecular union, it could be employed for determining the valency of elements.

F. S. K.

Kinetic Nature of Osmotic Pressure. By G. BREDIG (*Zeit. physikal. Chem.*, **4**, 444—456).—In replying to certain objections raised by Pupin against the Van't Hoff theory of osmotic pressure (Abstr., 1888, 778), the author develops an equation for the behaviour of a dissolved substance which is similar to that of Van der Waals for the behaviour of gases. A special point of interest is, that account is taken of the presence and specific attraction of the solvent, and in this way an explanation of the mechanism of solution is obtained, which, it is claimed, is of wider application than that of Nernst (this vol., p. 3), in which this attraction is neglected.

H. C.

Sphere of Action of Molecular Forces. By B. GALITZINE (*Zeit. physikal. Chem.*, **4**, 417—426).—By a process of theoretical reasoning similar to that already employed by Van der Waals, and using data given by Nadeschdin for several of the ethereal salts of the fatty acids in the critical condition, the author arrives at the conclusion that the sphere of action of the molecular forces is proportional to

the masses of the attracting molecules. He also concludes that the attraction is inversely proportional to the square of the distance.

H. C.

Fluid Crystals. By O. LEHMANN (*Zeit. physikal. Chem.*, **4**, 462—472).—Under the name of "fluid crystals," the author describes a cholesteryl benzoate first prepared by Reinitzer, which, although apparently melting at 145°, behaves between 145° and 178° towards polarised light as though still having crystalline structure. In other respects the substance is in a perfectly liquid condition between these temperatures.

H. C.

New Gas Burners. By M. GRÖGER (*Zeit. ang. Chem.*, 1889, 329—331).—These are in general form similar to Bunsen burners, but instead of having any means of regulating the entry of air at the bottom of the mixing tube, the top of the burner is made conical, and there is a screw arrangement by which a solid cone can be raised within, so as partially to close the opening. By this means a flame of any character can be obtained, from a luminous one to one approaching that of a blowpipe, whilst the size of the flame can be greatly reduced without altering its character, and without risk of its flashing down. A burner on the same principle giving a flat flame is also described.

M. J. S.

Inorganic Chemistry.

Hydrogen Peroxide. By G. TAMMANN (*Zeit. physikal. Chem.*, **4**, 441—443).—The spontaneous decomposition of hydrogen peroxide in alkaline solution is found to be independent of the amount or nature of the base which is present. It appears probable from the author's experiments that it is really caused by the presence of traces of metallic oxides, such as the oxide of iron, dissolved in the alkali. It is shown that the addition of small quantities of such oxides increases enormously the rate of decomposition.

The freezing points of aqueous solutions of hydrogen peroxide were determined, and from these a molecular reduction of 8·79 was found. Hydrogen peroxide being a non-electrolyte, this number would correspond with the formula H_4O_4.

H. C.

Hydrochlorides of Chlorides. By R. ENGEL (*Bull. Soc. Chim.* [3], 1, 695—699).—A review of the known hydrochlorides of chlorides, and a discussion of their probable constitution.

T. G. N.

Iodic Acid. By H. LESCŒUR (*Bull. Soc. Chim.* [3], 1, 563).—The crystals of iodic acid deposited from its solution in dilute or moderately concentrated nitric acid are monohydrated, whereas those obtained from the solution of iodic acid in concentrated nitric acid

are anhydrous. The author thinks that the crystals deposited from solution in nitric acid of intermediate strength are mixtures of the hydrated and anhydrous varieties. T. G. N.

Iodic Acid; Double Salts of Iodic Acid with other Acids. By C. W. Blomstrand (*J. pr. Chem.* [2], **40**, 305—340; compare Abstr., 1887, 327).—In the oxygen-acids of phosphorus and iodine only one atom of oxygen is strongly united to the phosphorus and iodine, the radicles being $PO{\cdot}O$ and $IO{\cdot}O$ respectively, thus differing from the oxygen-acids of nitrogen, chlorine, and bromine, where two atoms of oxygen are equally strongly united to the nitrogen, chlorine, or bromine, the radicles being NO_2, ClO_2, and BrO_2 respectively.

In support of the above statement, the author has prepared double salts of iodic acid with other acids which may be regarded as condensation-products, requiring for their formation an extra-radicle oxygen atom, analogous to that which is allowed to exist in aldehyde and to be the cause of the easy polymerisation of that substance; thus, $C_2H_4{:}O + O{:}C_2H_4 = C_2H_4{:}O_2{:}C_2H_4$. The formula for iodic acid thus becomes $HO{\cdot}IO{:}O$.

Potassium sulphatoiodate was obtained by mixing potassium pyrosulphate (1 mol.) and iodate ($1\frac{1}{2}$ mol.) in concentrated solution, and its formula found to be identical with that of Marignac's salt $KO{\cdot}IO(OH){\cdot}O{\cdot}SO_2{\cdot}OK$.

Potassium molybdoiodate, $KO{\cdot}IO(OH){\cdot}O{\cdot}MoO_2{\cdot}OH + H_2O$, is obtained as a white precipitate on adding a concentrated solution of potassium nitrate to a solution of sodium molybdate and iodic acid in nitric acid; it crystallises with difficulty in short needles, and is sparingly soluble in water. *Ammonium molybdoiodate* is obtained in the same way, and has similar properties, but contains no water of crystallisation. The *thallium* and *lead* salts were obtained. *Molybdoiodic acid* is obtained as a yellowish, transparent mass on evaporating the solution formed by the action of dilute sulphuric acid on a mixture of barium iodate and molybdate. Several of its reactions with inorganic and organic salts are given.

Potassium tungstoiodate, $KO{\cdot}WO_2{\cdot}O{\cdot}IO(OH)OK + H_2O$, is obtained by adding, by degrees, a solution of iodic acid to one of potassium tungstate; after some hours, a crystalline magma is obtained, more than 90 per cent. of which consists of slender needles of the tungstoiodate, the rest being tabular crystals of acid tungstate.

Potassium chromoiodate has been described by Berg (Abstr., 1887, 776); the author's analyses of this salt leave some doubt both as to the amount of water it contains and as to its formula.

The author has also obtained an *ammonium triiodate*,

$$NH_4O{\cdot}IO(OH){\cdot}O{\cdot}IO(OH){\cdot}O{\cdot}IO_2,$$

of which the crystallography is given, and a *sodium triiodate*, $NaO{\cdot}IO(OH){\cdot}O{\cdot}IO(OH){\cdot}O{\cdot}IO_2 + \frac{1}{2}H_2O$. A. G. B.

Specific Gravity of Ammonia Solutions. By G. Lunge and T. Wiernik (*Zeit. ang. Chem.*, 1889, 181—183).—The authors have redetermined with extreme care the sp. gr., referred to water at 15°, percentage of ammonia, and coefficient of expansion of ammonia

solutions of 24 different strengths. The following is an abstract of their table:—

Specific gravity at 15°.	Percentage of NH_3.	Correction of the sp. gr. for ± 1°.	Specific gravity at 15°.	Percentage of NH_3.	Correction of the sp. gr. for ± 1°.
0·990	2·31	0·00020	0·930	18·64	0·00042
0·980	4·80	0·00023	0·920	21·75	0·00047
0·970	7·31	0·00025	0·910	24·99	0·00052
0·960	9·91	0·00029	0·900	28·33	0·00057
0·950	12·74	0·00034	0·890	31·75	0·00061
0·940	15·63	0·00039	0·880	35·60	—

M. J. S.

A Derivative of Boric and Phosphoric Acids. By G. MEYER (*Ber.*, **22**, 2919).—When a mixture of boric and phosphoric acids is heated to redness, a very inert, white substance, PO_4B, is formed. It reddens moist litmus paper, but seems not to be dissolved by boiling water, and only to be very slowly attacked by boiling aqueous alkalis. Fusion with alkalis or alkaline carbonates causes instant decomposition, and fusion with sodium chloride also yields a soluble melt.
L. T. T.

Silicon. By E. P. HARRIS (*Chem. Cent.*, 1889, ii, 283—284).—The author has successfully prepared silicon by means of Gatterman's method, ignition of fine sand with magnesium powder, and in addition to the already known halogen-derivatives, he has prepared a *silicon nitride*, $NH_2\cdot SiN$, by acting on silicon chloride or silicon iodide with dry ammonia, whereby a considerable development of heat takes place. It is a snow-white powder. If the flux, obtained in the preparation of the silicon, be treated with dilute hydrochloric acid to dissolve out the magnesium oxide, silicon chloroform is obtained as a light, colourless, inflammable liquid, boiling at 42—44°.
J. W. L.

Preparation of the Chlorides of Silicon, Aluminium, &c. By H. N. WARREN (*Chem. News*, **60**, 158).—Iron alloys of silicon or aluminium are heated to redness in a clay crucible and a current of chlorine gas is passed into the mass, suitable means being adopted to collect the volatile products. With chlorine and silicon-iron, the ferric chloride is condensed first, then the silicon chloride; if hydrogen chloride is used instead of chlorine, the ferrous chloride formed remains in the crucible and silicon chloroform distils off. The aluminium chloride obtained from aluminium-iron is purified by mixing with iron borings and distilling, or if the aluminium-iron alloy is mixed with common salt previous to submitting it to the action of chlorine, a sublimate of aluminium sodium chloride is obtained.
D. A. L.

Combining Energy of Rubidium. By N. BEKETOFF (*Chem. Centr.*, 1889, ii, 245, from *Bull. Acad.*, *St. Pétersbourg* [2], **1**, 117—118). —*Preparation of the metal.*—Rubidium hydroxide is precipitated from

the sulphate by barium hydroxide, calcined in a silver dish, and heated with fine aluminium clippings in an iron cylinder in a furnace; the cylinder being connected with a glass tube by means of an iron tube. A mixture of 1 equivalent of rubidium hydroxide and $1\frac{1}{2}$ equivalents of aluminium gives the best results. From 113 grams of hydroxide and 31 grams of aluminium, 31 grams of very pure rubidium was obtained. J. W. L.

Potassium Plumbate. Crystalline Hydrated Thallic Oxide. By D. CARNEGIE (*Chem. News*, **60**, 113).—Potassium plumbate is formed when potassium plumbite, obtained by dissolving litharge in molten potash, is strongly heated, with free access of air, for some time. The colourless aqueous solution has strongly oxidising properties; it evolves chlorine with excess of dilute hydrochloric acid or with dilute sulphuric acid when the latter is added rapidly in excess, lead sulphate being also formed, the chlorine in this case being derived from the potassium chloride present as an impurity in the potash; when boiled with litharge, it yields lead peroxide and potassium plumbite; whilst with manganous sulphate it gives hydrated manganic oxide, and dilute sulphuric acid added slowly produces a brown precipitate of hydrated lead peroxide, PbO_2,H_2O.

Fused potash dissolves small quantities of thallic oxide, and the resulting yellow mass when treated with water yields a reddish-brown precipitate of the hydrated thallic oxide. If, however, the fusion is continued for some time, a mass of very light, glistening, microscopic, hexagonal plates is produced, of the composition $Tl_2O_3,3H_2O$; they are brown in colour but transmit yellow light. They are unaffected by a temperature of 340°, and are readily soluble in dilute hydrochloric and sulphuric acids, but generally a slight reduction to thallous salt takes place. D. A. L.

Influence of Hydrogen Chloride on the Solubility of Cuprous Chloride and of Lead Chloride. By R. ENGEL (*Bull. Soc. Chim.*, [3], 1, 693—695).—The amount of cuprous chloride dissolved by hydrochloric acid increases with the hydrogen chloride present. A saturated solution of cuprous chloride in hydrochloric acid when cooled to −40° deposits cuprous chloride crystals, no hydrochloride of cuprous chloride being formed.

The presence of hydrogen chloride at first determines a diminished solubility of lead chloride, and it is not until a considerable amount of hydrogen chloride is present that an increasing solubility obtains; this the author thinks is due to the formation of the soluble hydrochloride of lead chloride.

Solubility tables for each of the above salts in hydrochloric acid of various strengths are given. T. G. N.

Oxysulphides of Mercury. By T. POLECK (*Ber.*, **22**, 2859—2861; compare Poleck and Goercki, Abstr., 1888, 1166).—The author's further experiments have shown that the oxysulphides of mercury are not known, and that their existence is highly improbable.

F. S. K.

Aluminium Amalgam and its use in Thermochemistry. By J. B. BAILLE and C. FÉRY (*Ann. Chim. Phys.* [6], **17**, 246—256).—Aluminium amalgam was first described by one of the authors in 1875. Experiments in sealed tubes in an atmosphere of indifferent gas show that solution of aluminium by mercury proceeds more rapidly the higher the temperature, and is especially active at the boiling point of mercury. It is, however, the liquid metal and not its vapour which attacks the aluminium. The quantity of aluminium dissolved at first increases with the time, but attains a maximum at the end of about two hours; it is independent of the pressure inside the tube and of the extent of metallic surface in contact, but is proportional to the quantity of mercury present.

When the mercury cools, crystals of the amalgam separate as a thick paste on the surface; it has the composition Al_2Hg_3. In moist air it rapidly oxidises with formation of the hydroxide, $Al_2O(OH)_4$. It decomposes water at the ordinary temperature, the change being especially rapid with very thin sheets of aluminium amalgamated on the surface. It is attacked by nitric acid, which has no action on aluminium alone, and rapidly decomposes a solution of potassium hydroxide with evolution of hydrogen.

If aluminium amalgam is mixed with antimony amalgam, metallic antimony separates at the surface in small crystals, and after a time the aluminium oxidises, so that the mercury is obtained free from both metals. When, on the other hand, lead amalgam is added to the aluminium amalgam, the aluminium separates at the surface and is rapidly oxidised. This phenomenon is analogous to the expulsion of aluminium from its alloys with copper, tin, &c., by mixing the fused alloys with lead.

The action of moist air on amalgamated aluminium foil in the calorimeter was utilised for the determination of the heat of formation of aluminium oxide and the hydroxides. The results obtained were as follows:—Al_2O_3, 392·6 Cals.; $Al_2O(OH)_4$, 394·6 Cals.; $Al_2(OH)_6$, 395·6 Cals.

The formation of the aluminium amalgam and the displacement of the aluminium by lead are accompanied by no appreciable thermal disturbance. C. H. B.

Preparation of Manganese from Manganese Chloride and Magnesium. By E. GLATZEL (*Ber.*, **22**, 2857—2859).—Manganese can be prepared by heating a mixture of finely divided, anhydrous manganese chloride (100 grams) and dry, powdered potassium chloride (200 grams) in a covered Hessian crucible until it just melts, and then adding magnesium (15 grams) in portions of 3—4 grams, at intervals of 2—3 minutes; if the fused mass is too hot a very violent reaction occurs, and the contents of the crucible are thrown out. The crucible is covered again, heated more strongly, and then allowed to cool slowly in the furnace. The yield of manganese is 20—25 grams, the metal containing traces only of silica, and being quite free from magnesium.

The specific gravity of manganese, as the average of four determinations, was found to be 7·3921 at 22°. F. S. K.

Reduction of Ferric Bromide by Boiling. By L. L. DE KONINCK (*Zeit. ang. Chem.*, 1889, 149).—A solution of ferric bromide containing excess of bromine begins to show the presence of a ferrous salt as soon as the excess of bromine has been expelled by boiling. Ferric bromide, free from bromine and from ferrous salt, can only be obtained by passing air through the solution in the cold. The excess of bromine is very tenaciously retained. M. J. S.

Mineralogical Chemistry.

Native Lead in Sweden. By L. J. IGELSTRÖM (*Jahrb. f. Min.*, 1889, ii, Mem., 32—36).—The Pajsberg manganese and iron ore mine twenty years ago yielded small quantities of native lead. At the Sjö mine in Örebro, the author discovered on January 24, 1889, this rare native metal in the neotokite (black manganese silicate) in the form of small laminæ with brilliant lustre. It closely resembles electrolytically deposited lead. The neotokite occurs in dolomite, and is accompanied by specular iron ore. B. H. B.

Atacamite in Chili. By L. DARAPSKY (*Jahrb. f. Min.*, 1889, ii, Mem., 1—18).—The author gives a complete bibliography of the subject, as well as the results of his own investigations. On comparing the results of all the analyses published, it is found impossible to refer all the occurrences of atacamite to a typical formula, although the formula $CuCl_2,3CuO,3\frac{1}{2}H_2O$ is the closest approximation. The irregular development of the crystals and variations in the angles appear to indicate that atacamite is not a mineralogical unit, but, like the felspars, is composed of two or more members. The terminal members are believed to be $CuCl_2,3CuO,3H_2O$ and $CuCl_2,4CuO,6H_2O$.

With reference to the formation of atacamite, the author shows that processes producing a similar compound in the laboratory are impossible in nature. The only processes worthy of consideration are the formation by heating a mixture of basic copper nitrate and sodium chloride at 200°, or a mixture of the former with copper sulphate and sodium chloride at 100°. The presence of gypsum and calcite in the deposits and the intimate mixture of ferric oxide and cuprous oxide, however, clearly point to pyrites and similar minerals as the mother substances, which probably were highly decomposed before they came into contact with the salt of the sea-water. In all probability, the principal cementing material of the aqueous oxychloride is water, and it is impossible for atacamite to have been formed by a replacement of the water of hydration of the chloride by oxide. B. H. B.

Cerium and Yttrium Phosphates from South Norway. By C. W. BLOMSTRAND (*Jahrb. f. Min.*, 1889, ii, Ref. 44—46, from *Geol.*

Fören. i Stockholm förhandl., 9, 160.)—The author gives the results of analyses of monazite from Moss (light brown crystals), from Dillingsö (1. large fragments with crystal planes, and 2. small, prismatic crystals), from Moss (large, orange crystals), from Löuneby (large prismatic crystals, 1. brownish-yellow, and 2. ash-grey), from Arendal, from Narestö, and from Hvalö (1. large, yellowish-brown crystals, and 2. violet-brown lump). From the results of these nine analyses, the author concludes that the monazites are normal salts of tribasic phosphoric acid, with the excess of bases in combination with silicic acid. In conclusion, the author gives the results of two analyses of xenotime from Hvalö and from Narestö. B. H. B.

Pleonectite, a New Mineral from Sweden. By L. J. IGELSTRÖM (*Jahrb. f. Min.*, 1889, ii, Mem., 40—43).—At the Sjö mine, Örebro, this new mineral has been found in narrow veins in a mixture of hausmannite, rhodonite, and calcite. It occurs in association with arseniopleite. It has a greyish-white colour, a hardness of 4, and a vitreous lustre. It does not occur in crystals. A qualitative analysis indicated that the mineral is a chlorine-bearing lead antimonio-arsenate, with an inconsiderable proportion of water. In composition and appearance, it most closely resembles hedyphane, a mineral discovered by Breithaupt in 1830, but is distinguished from that mineral by its infusibility before the blowpipe. The suggested name is derived from πλεονεκτέω (to have more) in allusion to the antimony minerals already discovered in the Sjö mine. A quantitative analysis of pleonectite will subsequently be published. B. H. B.

Synthesis of Quartz, Corundum, &c. By W. BRUHNS (*Jahrb. f. Min.*, 1889, ii, Mem., 62—65).—By the investigations of Daubrée, St. Claire-Deville, Hautefeuille, De Chroustchoff, and Doelter, the action of fluorine as mineralising agent has been widely recognised. Whereas these investigators invariably worked with high temperatures, the author has succeeded in obtaining similar results with temperatures not exceeding 300°, and with high steam pressure. His apparatus consists of a firmly closed platinum crucible hermetically sealed in a steel case. By placing freshly precipitated ferric hydrate in the apparatus with ammonium fluoride, and heating for 10 hours at 250°, the author obtained crystallised ferric oxide. Freshly precipitated and ignited alumina, heated with water and a trace of ammonium fluoride for 10 hours at 300°, yielded hexagonal pyramids of corundum. Quartz crystals were obtained in a similar manner from amorphous silica. A remarkable result was obtained by acting with hydrofluoric acid on pulverised potash-felspar. The felspar employed was microcline, having the following percentage composition:—

SiO_2.	Al_2O_3.	K_2O.	Na_2O.	Total.
64·33	18·61	13·49	3·56	99·99

After heating for 53 hours with hydrofluoric acid at 300°, small crystals of tridymite were obtained; whilst the lid of the platinum vessel was covered with a crust of an isotropic regular compound of

silica, alumina, potash, and fluorine. Experiments made with the expectation of obtaining titanic anhydride, tin oxide, andalusite, and topaz were unsuccessful. Another experiment, in which powdered iron was mixed with ferric oxide, amorphous titanic anhydride, and hydrofluoric acid, yielded crystals of titaniferous iron and magnetite.

B. H. B.

Formation of Silicates. By J. LEMBERG (*Jahrb. f. Min.*, 1889, ii, Ref., 34—36; from *Zeit. deutsch. geol. Ges.*, **39**, 559).—By the action of solutions of various sodium silicates on kaolin at high temperatures, the author has obtained zeolites of the analcime series. In nature only one member of this series is known. By treatment with potassium salts, the analcimes obtained were converted into the corresponding members of the (anhydrous) leucite series. Of this series, too, only one member occurs in nature. Leucites containing a proportion of silica different from that of the mineral leucite, appear to be split up at a high temperature into orthoclase and leucite. By the action of kaolin on solutions of potassium carbonate or sodium carbonate, respectively, at a high temperature, a potassium-nepheline or cancrinite was formed; in both cases carbonic anhydride was also formed. This suggests a new source for carbonic anhydride in nature, kaolin itself being able to drive out the carbonic acid from the alkali carbonates. This change may also be effected if kaolin is mixed with calcium carbonate and subjected to the action of a hot solution of sodium chloride or potassium chloride, when calcium chloride is formed, and subsequently alkali carbonate, which acts on the kaolin. These reactions lead the author to speculate as to the genesis of cancrinite and analcime, and of felspar and elæolite in the presence of cancrinite.

B. H. B.

Mineralogy of the French Creek Mines. By J. EGERMAN (*Jahrb. f. Min.*, 1889, ii, Ref. 17—18).—In the shafts of a magnetite mine at French Creek, Pennsylvania, the following minerals have been met with: iron pyrites, copper pyrites, apophyllite, desmine, and garnet in large crystals, and small crystals of calcite, orthoclase, pyroxene, and aragonite; masses of pyrallolite and erythrite, and needles of byssolite in calcite. Perfect crystals of apophyllite, 14 mm. side, gave on analysis the following results:—

SiO_2.	CaO.	K_2O.	H_2O.	Total.	Sp. gr.
51·63	25·42	6·27	16·58	99·90	2·35

An analysis of the desmine gave—

SiO_2.	Al_2O_3.	CaO.	MgO.	K_2O.	H_2O.	Total.
58·00	13·40	7·80	1·40	1·03	18·30	99·93

B. H. B.

Calamine and Apophyllite from the United States. By J. EGERMAN (*Jahrb. f. Min.*, 1889, ii, Ref. 256; from *Proc. Acad. Nat. Sci. Philadelphia*, 1889, 32—35).—The author gives analyses of (I)

calamine from Friedensville, New Jersey, and of (II) apophyllite from St. Peters, Chester Co., Pennsylvania. The results are as follows:—

	SiO_2.	Fe_2O_3.	ZnO.	CaO.	K_2O.	H_2O.	Total.
I.	24·32	2·12	65·05	—	—	7·86	99·35
II.	51·63	—	—	25·42	6·25	16·58	99·88

The sp. gr. of the apophyllite is 2·35. B. H. B.

Anthochroite, a New Mineral from Sweden. By L. J. IGELSTRÖM (*Jahrb. f. Min.*, 1889, ii, Mem., 36—39).—At Jacobsberg, in Wermland, there are two mines, one yielding braunite, the other hausmannite. Both mines are in the same Archæan limestone surrounded by granulite. The new mineral is met with only in the braunite mine. It is obtained by dissolving the braunite in hydrochloric acid. The violet residue is anthochroite. It also occurs in association with garnet, idocrase, manganese-epidote, mica, and all the minerals known at this mine, and it is met with in narrow veins in the limestone. The grains are optically biaxial. The hardness is 5½, and the chemical composition as follows:—

SiO_2.	MnO.	CaO.	MgO.	Al_2O_3 and Fe_2O_3.	K_2O and Na_2O.	Total.
51·6	3·4	23·3	13·5	1·4	[6·8]	100·00

The mineral is thus a bisilicate of lime, magnesia, and manganese. Violan and richterite resemble it in composition, but not in appearance and optical properties. The name, derived from ἄνθος, flower, and χρῶμα, colour, is considered suitable on account of the brilliant colour of the new mineral and of the mixture in which it occurs.

B. H. B.

Tourmaline-bearing Copper Ores from Chili. By A. v. GRODDECK (*Jahrb. f. Min.*, 1889, ii, Ref. 113—115; from *Zeit. deutsch. geol. Ges.*, 1887, 239—266).—The association of tourmaline with Chilian copper ores has been previously noticed. The author has examined a series of ores from Tamaya, in which this association is well exhibited, the tourmaline occurring both in the sulphuretted and oxidised copper ores and also in the calcite and quartz gangue and in the spathose, quartzose, micaceous, and chloritic containing-rocks. The crystals are mostly 0·1 to 0·5 mm. in length, and are strongly pleochroïc. On analysis they yielded—

SiO_2.	Al_2O_3.	B_2O_3.	FeO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	F.	Total.
36·34	32·22	10·87	8·31	0·79	3·92	3·14	0·22	3·89	trace	99·70

B. H. B.

Natrolite from Monte Baldo. By G. LUZZATTO (*Jahrb. f. Min.*, 1889, ii, Ref. 28; from *Rivista di Mineralogia e Cristallografia italiana*, 4, 54—55).—Carefully selected, clear and transparent crystals gave on analysis the following results:—

SiO_2.	Al_2O_3.	Na_2O.	CaO.	H_2O.	Total.
47·16	26·76	16·18	0·28	9·57	99·95

These results correspond with the formula $Na_2Al_2Si_3O_{10} + 2H_2O$.

B. H. B.

Eruptive Rocks of the Rhone. By H. LENK (*Jahrb. f. Min.*, 1889, ii, Ref. 74—79; from *Sitzber. Würtzburger phys.-med. Ges.*, 1886).—The author gives the results of a microscopic examination of the constitution of the eruptive rocks of the Rhone. Eight analyses are given of the various rocks. The author distinguishes seven groups of these rocks:—1. phonolites; 2. glass basalts (limburgite); 3. nepheline basalts; 4. felspar basalts; 5. nepheline-plagioclase basalts (identical with basanite); 6. hornblende basalts; 7. dolorites.

B. H. B.

The Transcaspian Naphtha District. By H. SJÖGREN (*Jahrb. f. Min.*, 1889, ii, Ref. 102—105, from *Jahrb. k. k. geol. Reichsanst.*, **37**, 47—62).—The author has subjected the mud from the Baku mud volcanoes to careful examination, and found it to yield on analysis:—

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	MgO.	CaO.	K_2O.	Na_2O.	H_2O.	Total.
57·98	15·60	9·66	0·40	4·52	1·08	3·25	1·34	5·75	99·58

The microscopic investigation showed that the principal constituents were isotropic, glassy grains, frequently very impure, pure white and reddish-brown, isotropic grains, a pyroxenic mineral, green amphibole, felspar with and without twinning striation, quartz, calcite in rhombohedra, magnetite, and iron pyrites. The remainder of the paper deals with the geology of the district, the author concluding that the naphtha emanates from great depths.

B. H. B.

An undescribed Meteoric Iron from East Tennessee. By F. A. GENTH (*Jahrb. f. Min.*, 1889, ii, Ref. 42; from *Proc. Acad. Nat. Sciences of Philadelphia*).—This meteorite appears to have fallen in 1860 at a distance of 10 miles from Cleveland, East Tennessee. Its original weight was about 115½ kilos. The mean of three analyses gave—

Fe.	Ni.	Co.	Cu.	P.	S.	Total.	Sp. gr.
89·60	8·80	0·67	0·12	0·32	0·01	99·52	7·521

B. H. B.

Meteorites of Alfianello and Concepcion. By C. FRIEDHEIM (*Jahrb. f. Min.*, 1889, ii, Ref., 278—279; from *Sitz-Ber. d. k. preuss. Akad. Wiss. Berlin*, **13**, 345—367).—The analysis of the meteorite of Alfianello gave 7·92 per cent. nickel-iron (I), 7·78 troilite, 0·60 chrome-iron, 37·38 olivine (II), 46·29 bronzite and augite (III):—

	I.		II.	III.
Fe......	88·84	SiO_2......	34·92	53·86
Ni......	10·09	Al_2O_3.....	—	5·76
Co.....	1·07	FeO......	13·79	10·55
Mn....	0·26	CaO......	—	7·73
		MgO.....	51·26	21·68

These results differ considerably from those previously published by Maissen, Flight, and v. Foullon.

The meteorite that fell in 1880 between Nogayá and Concepcion

was briefly described by Websky and Daubrée. The complete analysis gave the results shown under IV, and that of the portion soluble in hydrochloric acid the results shown under V:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	Cr_2O_3.	MnO.	CaO.	MgO.	Alkalis.
IV.	27·22	2·35	30·64	0·38	0·09	2·56	19·24	0·18
V.	26·67	2·24	30·42	—	—	2·25	18·79	0·12

	Ni.	Co.	Cu.Sn.	Ignition.	Insoluble.
IV.	1·61		trace	14·47	—
V.	1·46	0·12	—	—	1·82

With ether, 0·21 per cent. of a yellow bituminous substance was extracted, which volatilised at 200°. When ignited in a current of oxygen the meteorite yielded carbonic anhydride (= 1·56 of carbon) and 14·03 per cent. of water. Treated with boiling water, 40 grams of the meteorite yielded (in grams)—

SO_3.	S_2O_2.	K_2O.	Na_2O.	MgO.	CaO.	Cl.
0·5001	0·0551	0·0059	0·0479	0·0750	0·1450	0·0009

There was also contained in the meteorite 3·27 per cent. of sulphur, 0·064 per cent. of phosphorus, 2·08 per cent. of sulphuric anhydride, and 0·034 per cent. of nitrogen. B. H. B.

Organic Chemistry.

Purification of Amyl Iodide. By H. MALBOT (*Bull. Soc. Chim.* [3], 1, 604).—Amyl iodide may be completely freed from the alcohol which distils over in its preparation by treatment with an equal volume of concentrated hydrochloric acid, which dissolves this impurity; the alcohol may be recovered by subsequently diluting the hydrochloric solution. T. G. N.

Carbonylhydroferrocyanic Acid and Carbonylferrocyanides. By J. A. MULLER (*Ann. Chim. Phys.* [6], **17**, 93—102).—The author has previously described a new class of ferrocyanides and ferricyanides in which the group CO is substituted for KCN (Abstr., 1887, 649). The crude violet precipitate (*loc. cit.*), which still contains ferrocyanide, is treated with a warm solution of potassium carbonate, the liquid filtered, and when cold slightly acidified with acetic acid and mixed with excess of lead acetate. After remaining for a day, the liquid is again filtered, the filtrate mixed with a slight excess of potassium carbonate, and boiled. The traces of lead which remain in the filtrate from the lead carbonate are removed by means of hydrogen sulphide, after slightly acidifying with acetic acid.

Carbonylhydroferrocyanic acid, $H_3FeCO(CN)_5$, is obtained by the action of hydrogen sulphide on the copper salt, and when the solu-

tion is evaporated over potassium hydroxide in the dark the acid separates in colourless, platy crystals with an acid taste and an astringent after-taste. It is acid to litmus, and decomposes alkaline carbonates. When the aqueous solution is boiled, the acid decomposes with formation of a violet-blue precipitate and evolution of a large quantity of hydrocyanic acid, but no carbonic anhydride is evolved, and neither formic acid nor ferrocyanide is formed.

The *sodium salt* is obtained in the same manner as the potassium salt (*loc. cit.*), and crystallises with 6 mols. H_2O in very pale-yellow, monoclinic needles which become anhydrous at 110°. The insoluble carbonylferrocyanides are obtained from the alkaline salts by double decomposition.

The *silver* salt, precipitated by excess of silver nitrate in presence of a small quantity of acetic acid, forms a white, curdy precipitate which rapidly becomes black even in the dark. After being washed with water, it contains no potassium. It is slightly soluble in dilute mineral acids with evolution of hydrocyanic acid, but is practically insoluble even in boiling acetic acid. Potassium hydroxide converts it into potassium carbonylferrocyanide and silver oxide. It retains water after being dried in a vacuum, and at 100° to 110° it slowly decomposes, still retaining a small quantity of water. At a dull red heat decomposition is rapid, cyanogen and hydrogen cyanide being evolved. If in the preparation of the salt the alkaline carbonylferrocyanide is in excess, the precipitate only becomes slightly grey, but it retains potassium nitrate and possibly some silver nitrate.

The *uranium* salt, $(UO_2)_3(FeCOCy_5)_2 + 5H_2O$, from uranium nitrate and the potassium salt, is an orange-yellow, gelatinous substance which retains no potassium, and is only slightly soluble in water, but somewhat more soluble in dilute acetic acid. At 70° it forms a ruby-red, granular solid, which re-acquires the yellow colour when powdered; at 110°, it becomes black and partially decomposes, but still retains a small quantity of water.

The *cobalt salt* forms a lilac precipitate which contains 3·5 mols. H_2O, and retains potassium even after prolonged washing, its composition being represented by the formula $(Co_{2\cdot77}K_{0\cdot23})FeCO(CN)_5$. It is slightly soluble in water and is decomposed by cold dilute nitric acid. In a dry vacuum or when gently heated, it is partially dehydrated and becomes deep-blue. This change takes place even in boiling water, but the salt is rehydrated on cooling. It retains a small quantity of water even at 110°.

The *copper* salt forms a yellowish-green, gelatinous precipitate insoluble in dilute nitric or sulphuric acid. It retains no potassium, becomes dehydrated with change of colour when gently heated, and at 110° forms a somewhat hygroscopic, dark-brown powder, which undergoes slight decomposition at this temperature but still retains a small quantity of water.

The *ferric* salt is obtained from the potassium salt and ferric chloride as a violet precipitate which is free from potassium, and when dried at a moderate temperature forms a very friable resinous mass with a brilliant conchoidal fracture of very high metallic lustre. It alters even below 100°, and undergoes profound change at 100° to

110°. After being dried in a vacuum, it retains 12 to 13 per cent. of water. The violet precipitate dissolves in an aqueous solution of oxalic acid, forming a solution with a magnificent violet colour, but it is not soluble in acetic, lactic, succinic, tartaric, or citric acid. It dissolves, however, in solutions of the normal salts of these acids even in presence of a small quantity of free acid. The solutions are almost colourless or have only a slight violet tinge, but on the addition of sulphuric acid carbonylferrocyanide is again formed, and is precipitated or remains in solution according to the nature of the acid present. The violet precipitate of the ferric salt is not soluble in solutions of potassium chloride or nitrate, or in very dilute phosphoric or sulphuric acid, but is distinctly soluble in solutions of sodium hydrogen phosphate. It is slightly decomposed by potassium sulphate, and the liquid becomes acid; it decomposes potassium hydrogen carbonate even at 25°, carbonic anhydride being evolved. Analysis of the salt shows that it contains more ferric iron than is required by the formula, a result probably due to the presence of ferric oxide which was contained in the ferric chloride solution used in the preparation of the salt and cannot be removed by washing. Precipitation of the alkaline salt with ferric chloride solution of known strength, followed by a determination of the iron in the filtrate, also showed that the amount of iron precipitated was greater than the calculated quantity.

All these results point to the existence of a trivalent acidic radicle of the formula $FeCO(CN)_5$. The insoluble carbonylferrocyanides resemble the insoluble ferrocyanides in retaining small quantities of water which cannot be expelled without decomposing the salt.

C. H. B.

Note by Abstractor.—It is interesting to compare the properties of ferric carbonylferrocyanide with those of soluble Prussian-blue (Guignet, Abstr., 1889, 475). C. H. B.

Vinyl Alcohol, a Constant Constituent of Ethyl Ether. By T. POLECK and K. THÜMMEL (*Ber.*, **22**, 2863—2880).—When a solution of mercury oxychloride in pure sodium or potassium carbonate is shaken for 10—20 minutes with ether from the most varied sources, a yellowish-white, amorphous precipitate is always produced in small quantities, varying from 0·89—6·64 per cent. The samples employed had generally a neutral reaction, liberated iodine from a solution of potassium iodide, gave a brown coloration with potash, and were free from acetaldehyde; after having been shaken with the mercury solution, the ether gave no coloration with potash.

The white precipitate has the composition $CH_2\colon CH{\cdot}OHg{\cdot}O{\cdot}Hg_2Cl_2$, and may be named *vinyl oxymercurochloride*. It turns yellow at 100°, becoming colourless again on cooling, and at about 170° it swells up, like mercury thiocyanate, with evolution of a gas which burns with a blue flame. It is insoluble in water, alcohol, and ether; when freshly precipitated, it dissolves freely in hydrochloric acid, nitric acid, and hydrocyanic acid, but when dry it dissolves completely only on boiling even in concentrated hydrochloric acid. When boiled for a long time with potash, it is converted into a greenish-black powder which is in-

soluble in potash, and the alkaline solution contains a colourless compound which is precipitated on adding nitric acid.

The greenish-black compound has the composition

$$CH:C\cdot Hg_2(OH)_2,Hg_2(OH)_2,$$

and is named "*acetylenemercury*." It dissolves in concentrated acetic acid, forming a crystalline acetate, and it is soluble in nitric acid and in aqua regia, but insoluble in hydrochloric acid. It explodes very violently when heated (at about 157°), but not by percussion. The *acetate*, $CH:C\cdot Hg_2(OAc)_2,Hg(OAc)_2$, is obtained when the black powder is dissolved in concentrated acetic acid, and the filtered solution evaporated. It decomposes at 100°, or when boiled with water, and it is insoluble in ether and acids, except acetic acid; if the acetic acid solution is diluted, a colourless compound is precipitated and mercury remains in solution. When hydrogen sulphide is passed into the acetic acid solution, a yellowish or colourless precipitate is produced, and the precipitate turns greenish-black after some days. The acetate is decomposed by warm potash, being reconverted into the black, explosive compound.

The colourless compound which is precipitated on adding nitric acid to the alkaline solution of vinyl oxymercurochloride (see above) has the composition $CH:C\cdot HgO,HgCl_2$, and is named *acetylenemercury oxychloride*. It is an amorphous powder, insoluble in hydrochloric acid, nitric acid, ammonia, and alkaline carbonates, but readily soluble in potash, yielding a solution which is coloured yellow by hydrogen sulphide; it is not explosive, and when heated it volatilises, leaving a carbonaceous residue.

When ether is distilled with phenylhydrazine, the distillate gives no coloration with potash, and no precipitate with the mercury solution; the residue contains ethylidene phenylhydrazine.

Vinyl oxymercurochloride (see above) is decomposed by bromine, yielding bromal hydrate or bromoform and formic acid, according to the length of time during which the reaction takes place. When treated with a solution of iodine in potassium iodide, this vinyl-compound gives iodoform, and when triturated with dry potassium iodide an energetic reaction takes place, the dark-coloured explosive substance being formed. If vinyl oxymercurochloride is suspended in water and treated with potassium iodide, the mixture turns yellow or greyish-green and the solution becomes strongly alkaline; on adding hydrochloric acid, a reddish-brown powder is precipitated. When excess of hydrogen sulphide is passed into water containing the vinyl-compound in suspension, γ-trithioacetaldehyde (m. p. 75—76°), identical with the compound obtained by Marckwald (Abstr., 1888, 127), is formed; a small quantity of a very volatile, unpleasant smelling oil, probably thioacetaldehyde (compare Marckwald, *loc. cit.*), is also produced. Vinyl oxymercurochloride is decomposed by ammonium sulphide, with separation of mercuric sulphide, yielding acetamide and probably also traces of thioacetamide. It is only slowly oxidised by chromic acid and potassium permanganate, yielding acetic acid, carbonic anhydride, and small quantities of formic acid.

When a large quantity of ether is repeatedly submitted to fractional

distillation, two liquids, boiling at 30—31° and 37—38° respectively, are obtained; both these liquids give a copious precipitate with the mercury solution, but they are generally obtained in small quantities only, owing to polymerisation taking place during the distillation. The lower boiling liquid has an ethereal odour and a neutral reaction, but it soon becomes acid, owing to the formation of acetic acid; it does not liberate iodine from potassium iodide until it has undergone oxidation, a fact which indicates the formation of hydrogen peroxide. The higher boiling liquid has a slight ethereal odour, does not alter on keeping, has a neutral reaction, and, unlike the lower boiling liquid, is not oxidised by potassium permanganate. An ammoniacal solution of silver nitrate is not reduced by either of the two liquids, but both give a brown coloration with potash; the lower boiling liquid only reduces alkaline copper solutions and yields iodoform with potassium iodide.

Vinyl ethyl ether gives a precipitate with the mercury solution referred to above, but the precipitate differs from vinyl oxymercurochloride in composition, and in not forming an explosive compound when treated with potash.

Vinyl chloride and vinyl iodide in alcoholic solution give precipitates from which explosive substances are obtained by treatment with potash.

The above experiments show that the substance, which is present in ether and which is precipitated by the mercury solution, is vinyl alcohol.

When air containing ozone is passed for a long time through pure ether, or when pure ether is shaken for a long time with hydrogen peroxide, it yields subsequently a precipitate of vinyl oxymercurochloride.

A violent reaction occurs when pure ether is added drop by drop to anhydrous chromic acid, a liquid distilling which, if the operation is carefully conducted, smells only slightly of ether, but has, on the other hand, a peculiar aldehyde-like odour. When the distillate is fractionated, a liquid boiling at 33°, probably a polymeride of vinyl alcohol, is obtained. It has a neutral reaction, does not liberate iodine from potassium iodide, and does not give a brown coloration with potash, but it yields a copious precipitate with the mercury solution; it resembles the liquid boiling at 37—38° (see above) in its other properties.

Vinyl alcohol and hydrogen peroxide are formed when pure ether is exposed to direct sunlight either alone or in contact with water; the presence of hydrogen peroxide can be recognised by the chromic acid reaction.

Commercial ether gives only a slight blue coloration with dilute chromic acid solution, but on agitating with air an intense blue coloration is produced. The formation of hydrogen peroxide in this way accounts for the explosions which sometimes occur when ether, which has been kept for a long time, is distilled. F. S. K.

Synthesis of some Glycerols by means of Hypochlorous Acid. By S. REFORMATZKY (*J. pr. Chem.* [2], **40**, 396—419; compare Abstr., 1885, 882).—A *chlorhydrin*, $C_6H_{13}O_2Cl$, is obtained on adding, by

degrees, a solution of hypochlorous acid free from chlorine to allyl dimethyl carbinol (20 grams), and some ice-water, in a retort, cooled by ice (compare Orloff, Abstr., 1886, 138, 681). When the odour of hypochlorous acid has nearly disappeared, a little sodium thiosulphate is added to destroy the last traces of it, the liquid is filtered, and then shaken with ether, which extracts the chlorhydrin (23 grams); it is a thick liquid.

To obtain the corresponding *glycerol*, $C_6H_{14}O_3$, potassium hydroxide (25 grams) is added to the residue in the retort, without previously extracting the chlorhydrin, and the mixture is distilled until two-thirds have passed over; the residue is nearly all evaporated in a dish, the excess of potassium hydroxide neutralised with sulphuric acid, and the excess of the latter with dry sodium carbonate; evaporation is then continued to dryness, and the residue extracted with 95 per cent. alcohol; the solution is mixed with ether, which throws down foreign matters, and then evaporated to obtain the glycerol (80 per cent. of theory). It distils at about 198° at a pressure of 60—65 mm., and is a colourless, sweet, thick liquid, soluble in water and alcohol but not in ether. The *acetate*, $C_6H_{11}(OAc)_3$, is obtained by heating the glycerol (3 grams) with acetic anhydride (9 grams) at 100° in a tube for 10 hours, and evaporating off the excess of the latter; it is a mobile liquid insoluble in water, soluble in alcohol and ether.

When oxidised by nitric acid, the glycerol yields a triatomic monobasic acid containing 6 atoms of carbon. Potassium permanganate oxidises the glycerol to hydroxyvaleric acid.

A *chlorhydrin*, $C_8H_{12}ClO_2$, is prepared from allyl diethyl carbinol in the same way as from allyl dimethyl carbinol, and from this the corresponding *glycerol*, $C_8H_{15}(OH)_3$, is obtained; it is a colourless, thick, bitter liquid, soluble in water, alcohol, and ether, and boiling at 204—207° under 55—60 mm. pressure. An *acetyl-derivative*, $C_8H_{15}O_3Ac_3$, was obtained.

Allyl methyl propyl carbinol yields a *chlorhydrin*, $C_8H_{15}(OH)_2Cl$, as a somewhat thick, colourless liquid. The corresponding *glycerol*, $C_8H_{15}(OH)_3$, is a thick, colourless liquid, easily soluble in water and alcohol, sparingly in ether, and boiling at 210° under 60 mm. pressure. An *acetyl-derivative* was obtained.

Unsuccessful attempts were made to prepare a glycerol from allyl dipropyl carbinol, and a glycerol by the hydrolysis of diallyl carbinol by cold sulphuric acid.

A *chlorhydrin*, $C_7H_{11}(OH)_3Cl_2$, was obtained from diallyl carbinol by the action of hypochlorous acid, but it gave no glycerol.

A. G. B.

Identity of Brain Sugar with Galactose. By H. THIERFELDER (*Zeit. physiol. Chem.*, **14**, 209—216; compare Brown and Morris, Trans., 1890, **57**, 57).—Bäyer and Liebrich (*Virchow's Arch.*, **39**, 183) first described a carbohydrate in the brain which they obtained from protagon. Since then, Otto (*ibid.*, **41**, 272), Geoghegan (*Zeit. physiol. Chem.*, **3**, 337), and Thudichum (Abstr., 1882, 537) obtained one by treating cerebrin with hydrochloric acid. The last-named observer prepared it in a crystalline form, and termed it cerebrose. In the present research, the sugar was prepared from

cerebrin by the action of 2 per cent. sulphuric acid. It reduces Fehling's solution, yields mucic acid on oxidation with nitric acid, and thus resembles galactose, which is the only glucose that yields mucic acid on this treatment. In its melting point, specific rotation, fermentation, and phenylhydrazine-compound, its properties are also the same as those of galactose. The mother substance of this sugar in the brain has yet to be isolated. W. D. H.

Eucalyptus Honey. By MAQUENNE (*Ann. Chim. Phys.* [6], **17**, 495—500).—Eucalyptus honey is secreted by a peculiar species of black bee, which constructs enormous hives on the summits of the gigantic *Eucalypti* of Australia. Some of these hives furnish as much as 5000 kilos. of crude honey each. It is a thick syrup, similar in appearance to ordinary honey but containing a somewhat smaller proportion of crystals, and it has a strong aromatic odour. It consists essentially of levulose and dextrose in practically the same proportions as in invert sugar, with a small quantity of aromatic substances, and traces of gum insoluble in alcohol. No peculiar sugar could be detected. C. H. B.

The Precipitation of Colloïd Carbohydrates by Salts. By J. POHL (*Zeit. physiol. Chem.*, **14**, 151—164).—The neutral salts used in the separation of proteïds can also be employed for the separation of plant mucilages and other colloïd carbohydrates. Those examined in the present research can be grouped as follows:—

A. Those not precipitable by saturation with neutral salts:—Gum arabic and sodium arabinate.

B. Those precipitable by saturation with ammonium sulphate:—The mucilages of tragacanth, althea, linseed, and cydonia. Gum tragacanth is also distinguishable from gum arabic by its lesser solubilities. Cydonia mucilage is a mixture of cellulose, and a carbohydrate very like gum tragacanth.

C. Those precipitable by saturation with ammonium sulphate, ammonium phosphate, and potassium acetate:—Carragheen mucilage.

D. Those precipitable by saturation with sodium sulphate, magnesium sulphate, ammonium sulphate, and ammonium phosphate:—Solnble starch, lichen starch, dextrin, salep mucilage, and pectin. These forms of carbohydrates are further distinguished by the percentage of salt necessary for the commencement of precipitation; thus tragacanth requires complete saturation with ammonium sulphate for its precipitation, that is, 53·5 grams of salt to every 100 c.c. of solution. Salep mucilage begins to be precipitated by 40·4 grams, and soluble starch by 24·1 grams of the same salt per 100 c.c. of solution. Further, by fractional precipitation with magnesium sulphate, salep mucilage can be differentiated into two varieties, named α and β. These two varieties further differ in the melting-points of their phenylhydrazine-compounds. W. D. H.

Oxalenediamidoxime and Oxaleneanilidoximamidoxime. By W. ZINKEISEN (*Ber.*, **22**, 2946—2957.)—*Oxalenediamidoxime*, $OH\cdot N:C(NH_2)\cdot C(NH_2):N\cdot OH$, is prepared by gradually adding cyananiline (100 parts) to a solution of hydroxylamine hydrochloride

(50 parts) in 90 per cent. alcohol (500 parts). The amount of sodium carbonate necessary to liberate the hydroxylamine is then added, and the whole filtered from the sodium chloride. The filtrate is evaporated down a little, well shaken when cold, and left for some hours; the diamidoxime which separates is dissolved in boiling water, and boiled with animal charcoal. It crystallises in dazzling, white, concentrically-grouped lanceolate crystals, melts at 196° (uncorr.), with evolution of gas, is sparingly soluble in alcohol, insoluble in ether, chloroform, benzene, and light petroleum, readily soluble in hot water; it dissolves in acids and bases. The aqueous solution, with copper sulphate, ferric chloride, and Fehling's solution gives a grass-green, flaky precipitate, a deep brownish-red coloration, and a dirty precipitate respectively. The *hydrochloride* forms slender, colourless prisms, insoluble in absolute alcohol and ether. The *dibenzoyl-derivative*, $C_{16}H_{14}N_4O_4$, obtained by gradually adding the finely-powdered dioxime to hot benzoic chloride, crystallises in slender, slightly-yellow plates, melts at 217°, is insoluble in water, ether, benzene, and light petroleum, readily soluble in chloroform, sparingly in alcohol. It is insoluble in hydrochloric acid and in alkali, but dissolves unchanged in acetic and in cold strong sulphuric acids.

Oxalenediazoximedibenzyl, $CPh\ll{}^{N—}_{O\cdot N}\gg C\cdot C\ll{}^{—N}_{N\cdot O}\gg CPh$, is formed when oxalenediamidoxime is heated for a long time with an excess of benzoic chloride. It crystallises from chloroform in slender, white needles, melts at 246°, is soluble in benzene, insoluble in water, alcohol, ether, and in strong hydrochloric acid and alkalis; but readily soluble in strong sulphuric and acetic acids. When heated above its melting point, it sublimes without decomposition.

Diacetyloxalenediamidoxime, $C_6H_{10}N_4O_4$, prepared by gradually adding the powdered diamidoxime to boiling acetic anhydride, crystallises in needles, melts at 184—187°, dissolves readily in alcohol, sparingly in benzene, and is insoluble in chloroform, ether, and light petroleum. Acids and bases readily decompose it. When heated for a long time with acetic anhydride, *oxalenediazoximediethenyl*, $C_6H_6N_4O_2$, is obtained. This crystallises in colourless needles, melts at 164—165°, dissolves in alcohol and chloroform, less readily in hot water and benzene; and is insoluble in ether and light petroleum. It sublimes in long, slender needles.

Oxalenediamidoxime diethyl ether, $OEt\cdot N\colon C(NH_2)\cdot C(NH_2)\colon N\cdot OEt$, is prepared by boiling an alcoholic solution of oxalenediamidoxime (1 mol.) with ethyl iodide (2 mols.) and the calculated amount of sodium ethoxide for three hours in a reflux apparatus, evaporating the whole to half its original bulk, treating with water, and filtering. It is washed several times with water, dissolved in boiling alcohol, and sufficient water added to produce a slight turbidity. It crystallises in slender, colourless, matted needles, melts at 114—115°, dissolves readily in alcohol, ether, chloroform, and benzene, sparingly in hot water. The hydrochloride crystallises well.

Oxalenediazoximedipropenyldicarboxylic acid,

$$COOH\cdot C_2H_4\cdot C\ll{}^{N—}_{O\cdot N}\gg C\cdot C\ll{}^{—N}_{N\cdot O}\gg C\cdot C_2H_4\cdot COOH,$$

is obtained by heating an intimate mixture of oxalenediamidoxime (1 mol.) and succinic anhydride (2 mols.) at 140—150°, dissolving the product in hot, dilute aqueous soda, and precipitating with hydrochloric acid. It crystallises from boiling water in almost colourless needles, melts at 200°, dissolves sparingly in hot water, readily in alcohol and chloroform, and is insoluble in ether and benzene. The alkali salts are readily soluble in water.

Oxalenediuramidoxime,

$$OH\cdot N{:}C(NH\cdot CO\cdot NH_2)\cdot C(NH\cdot CO\cdot NH_2){:}N\cdot OH,$$

prepared by adding a saturated solution of potassium cyanide (2 mols.) to a hydrochloric acid solution of oxalenediamidoxime (1 mol.), crystallises from very dilute alcohol in slender, white needles, melts at 191—192° with decomposition, dissolves sparingly in hot water, readily in alcohol, and is insoluble in ether, benzene, and chloroform. Both acids and bases dissolve it readily.

Ethyl oxalenediamidoxime dicarbonate, $C_8H_{14}N_4O_6$, is formed when finely powdered, dry oxalenediamidoxime (1 mol.) is slightly heated on a water-bath with ethyl chlorocarbonate for 20 minutes. It crystallises from water in long, thin needles, melting at 168°; it is sparingly soluble in hot water, and soluble in alcohol, ether, and in acids and bases.

Oxaleneanilidoximamidoxime, $OH\cdot N{:}C(NHPh)\cdot C(NHPh){:}N\cdot OH$, is formed as bye-product in the action of cyananiline on hydroxylamine, and is best prepared by gradually adding solid cyananiline to an alcoholic solution of hydroxylamine hydrochloride (2 mols.), filtering from the ammonium chloride, and evaporating down until crystals separate. When cold it is again filtered from the oxalenediamidoxime, and evaporated almost to dryness. The crystals which separate after a long time are crystallised from boiling water. It forms colourless, hexagonal plates, melts at 180°, and has almost exactly the same properties as oxalenediamidoxime, except that it dissolves more readily in alcohol, and seems to be less stable. The precipitate with copper sulphate has a less pure colour than that which the diamidoxime gives. The *hydrochloride* crystallises in slender, colourless needles, which become green when exposed to air. The *dibenzoyl-derivative*, $C_{22}H_{18}N_4O_4$, prepared by heating oxaleneanilidoximamidoxime (1 mol.) with benzoic chloride (2 mols.) on a water-bath, crystallises from dilute alcohol in slender, slightly-yellow, matted needles, melts at 189°, is insoluble in water and light petroleum, soluble in alcohol, benzene, and chloroform. When boiled with alkalis, it is gradually decomposed, but does not change when boiled for a short time with hydrochloric acid.

Oxaleneanilidoximazoxime ethenyl, $OH\cdot N{:}C(NHPh)\cdot C{<}^{N}_{N\cdot O}{>}CMe$, is obtained by dissolving oxaleneanilidoximamidoxime in hot acetic anhydride, filtering when cold, washing repeatedly with cold water, and dissolving in boiling water containing a little alcohol. It crystallises in slender, colourless needles, melts at 172°, dissolves in alcohol, ether, and benzene, rather sparingly in hot water. It is dissolved by both acids and bases, and is less stable than the double azoxime obtained from oxalenediamidoxime. N. H. M.

Succinenediamidoxime. By F. SEMBRITZKI (*Ber.*, **22**, 2958—2967).—*Succinenediamidoxime*,

$$OH\cdot N\colon C(NH_2)\cdot CH_2\cdot CH_2\cdot C(NH_2)\colon N\cdot OH,$$

is prepared by adding a strong solution of hydroxylamine hydrochloride (2 mols.) and sodium carbonate (1 mol.) to an alcoholic solution of ethylene dicyanide (1 mol.), and keeping the mixture for three or four days in a well-closed vessel. It is then filtered from the crystals of the diamidoxime and sodium chloride, and left to evaporate in a warm place. The sodium chloride is dissolved in cold water, and the remaining diamidoxime recrystallised from hot water. It forms transparent, monoclinic crystals, $a : b : c = 1{\cdot}2744 : 1 : 0{\cdot}9269$; $\beta = 79° 50'$, melts at 188°, with evolution of ammonia, and is sparingly soluble in hot alcohol, insoluble in cold water, ether, acetone, benzene, and chloroform. It yields salts with acids and with bases; the *hydrochloride* is white, and dissolves in absolute alcohol; the *copper salt* is bright-green; the *silver salt* is white, but at once becomes dark when exposed to light, and is completely reduced when heated, with formation of a silver mirror. The *dibenzoyl-derivative*, $C_{18}H_{18}N_4O_4$, crystallises from amyl alcohol in small, white needles, melts at 192°, is insoluble in water, alcohol, ether, chloroform, and benzene, &c., and does not unite with acids and alkalis.

Succinenediazoximedibenzenyl,

$$CPh{<}^{O\cdot N}_{N\text{——}}{>}C\cdot CH_2\cdot CH_2\cdot C{<}^{N\cdot O}_{\text{——}N}{>}CPh,$$

is obtained when the above dibenzoyl-derivative is heated with water for five hours at 150—160°. It crystallises in needles, melts at 158—159°, is soluble in benzene and hot alcohol, sparingly soluble in ether, insoluble in water, light petroleum, and chloroform.

Diacetylsuccinenediamidoxime, $C_8H_{14}N_4O_4$, crystallises from absolute alcohol in white, monoclinic scales, $a : b : c = 1{\cdot}2998 : 1 : 0{\cdot}9105$; $\beta = 82° 58'$; it melts at 167—168°, is soluble in hot water and in acids, insoluble in ether, benzene, and in alkalis. The *diethyl salt*, $OEt\cdot N\colon C(NH_2)\cdot CH_2\cdot CH_2\cdot C(NH_2)\colon N\cdot OEt$, prepared by digesting the equivalent amounts of succinenediamidoxime, sodium ethoxide, and ethyl iodide for some hours, crystallises in colourless needles, melts at 119°, dissolves readily in water, alcohol, ether, and chloroform, is insoluble in light petroleum, and is soluble in acids, but not in alkalis.

Succinenediuramidoxime, $C_6H_{12}N_6O_4$, is readily obtained by mixing concentrated aqueous solutions of the hydrochloride of the diamidoxime and potassium cyanate. It crystallises, with 2 mols. H_2O, in needles which soften at 100—105°; the anhydrous salt melts at 163·5 with decomposition, is soluble in hot water, insoluble in cold water, alcohol, ether, and benzene, &c., unites readily with acids, but is sparingly soluble in cold alkalis.

Succineneimidodioxime, $\begin{matrix} CH_2\cdot C(N\cdot OH) \\ | \\ CH_2\cdot C(N\cdot OH) \end{matrix}{>}NH$, is formed in small quantity in the preparation of succinenediamidoxime, but is obtained alone when the mixture is digested for several days at 60—70°. It

crystallises with 2 mols. H_2O, and resembles the diamidoxime in its properties and solubility. When dissolved in aqueous potash, the solution becomes first blue, then green. With ferric chloride, a dark-violet coloration is produced. The *copper salt* is dirty green; the *silver salt*, $C_4H_5N_3O_2Ag_2$, forms small, lustrous plates which detonate when heated, leaving a residue of silver. The *dibenzoyl-derivative*, $C_{18}H_{15}N_3O_4$, melts at 187—189° with previous blackening, is soluble in benzene and hot alcohol, insoluble in water, ether, and chloroform, does not unite with acids, but dissolves in hot alkalis with decomposition. The *diacetyl-derivative*, $C_8H_{11}N_3O_4$, is a white, crystalline powder, melts at 170—171°, dissolves in water, alcohol, ether, and chloroform, sparingly in benzene, and is insoluble in light petroleum. N. H. M.

Glutarenediamidoxime and its Derivatives. By J. BIEDERMANN (*Ber.*, **22**, 2967—2973).—Trimethylene cyanide is conveniently prepared by digesting trimethylene bromide dissolved in 96 per cent. alcohol (5 parts) with a slight excess of finely powdered potassium cyanide for eight hours on a water-bath, filtering, and distilling off five-sixths of the alcohol. The residue is treated with an equal volume of ether. The ethereal alcoholic layer is separated from the aqueous, evaporated down, and the resulting yellowish oil distilled under diminished pressure.

Glutarenediamidoxime, $CH_2[CH_2\cdot C(NH_2)\colon N\cdot OH]_2$, is obtained, together with glutarenimidodioxime, when equivalent amounts of hydroxylamine hydrochloride, sodium carbonate, and trimethylene dicyanide, dissolved in aqueous alcohol, are digested for 10 hours at 60—70°. A part of the diamidoxime separates on cooling. The mother liquor is evaporated to dryness, extracted with boiling water, the solution allowed to cool, filtered, and again evaporated to dryness. The residue now consists of sodium chloride, glutarenimidodioxime, and a small amount of the diamidoxime. Glutarenediamidoxime crystallises from water in well-formed, lustrous prisms (with 1 mol. H_2O), dissolves readily in hot water and alcohol, less in ether and chloroform, and is dissolved by acids and bases. It gives a reddish-brown coloration with ferric chloride. The *diacetyl-derivative*, $C_9H_{16}N_4O_4$, crystallises in microscopic, slender, colourless needles, melts at 115°, and is readily soluble in hot water and alcohol, insoluble in ether, chloroform, benzene, &c.

Glutarenediazoximediethenyl, $CH_2(CH_2\cdot C{<}^{N\cdot O}_{\text{—}N}{>}CMe)_2$, is prepared by boiling a solution of glutarenediamidoxime in acetic anhydride, evaporating down, dissolving the crystals which separate in benzene, and precipitating with light petroleum. It forms slender, colourless needles, melting at 138—139°.

Glutarenimidodioxime, $NH{<}^{C(N\cdot OH)\cdot CH_2}_{C(N\cdot OH)\cdot CH_2}{>}CH_2$, is obtained by extracting the residue from the preparation of the diamidoxime with hot absolute alcohol; the solution is evaporated, and the residue dissolved in chloroform and precipitated with light petroleum. It melts at 193° without decomposition, is very sparingly soluble in

alcohol, ether, and chloroform, insoluble in benzene and light petroleum, soluble in both acids and alkalis, and gives a red-violet coloration with ferric chloride. The *picrate* crystallises from alcohol in splendid, yellow needles, melting at 175° with decomposition; the *hydrochloride* forms white needles. The *diacetyl-compound*, $C_9H_{13}N_3O_4$, is a white, crystalline powder, melts at 127°, is readily soluble in water, alcohol, ether, and chloroform, sparingly in benzene, and is readily dissolved by acids and alkalis. The *benzoyl-compound*, $C_{19}H_{17}N_3O_4$, crystallises in stellate groups of needles, melts at 179—180°, is soluble in hot alcohol and benzene, almost insoluble in water, ether, and chloroform.

When trimethylene dicyanide is treated with hydroxylamine (1 mol.) at the ordinary temperature, a compound having the formula $C_5H_9N_3O$ (which is the formula of γ-cyanobutenylamidoxime) is obtained. It crystallises in colourless needles, melts at 103°, is readily soluble in hot water and alcohol, very sparingly in ether, chloroform, and benzene. With ferric chloride it gives a red coloration, but neither Fehling's solution, silver nitrate, nor lead acetate gives a precipitate. It has only basic properties, being insoluble in alkalis.

N. H. M.

Hydroxamic Acids of the Fatty Series. By C. HOFFMANN (*Ber.*, **22**, 2854—2856).—*Acetohydroxamic acid*, OH·CMe:NOH, and not ethenylamidoxime, as previously stated (compare Abstr., 1887, 911), is formed when acetamide (1 mol.) is treated with hydroxylamine hydrochloride (1 mol.) in cold, concentrated, aqueous solution. The mixture is kept until it no longer reduces Fehling's solution, then acidified with acetic acid, and mixed with excess of copper acetate; the precipitated copper salt is washed, suspended in alcohol, decomposed with hydrogen sulphide, and the filtrate evaporated. It separates from dilute alcohol and hot water in crystals containing $\frac{1}{2}$ mol. H_2O, melts at about 58—59°, and is very readily soluble in water and alcohol, but insoluble in ether. It loses its water over sulphuric acid under reduced pressure, and then melts at 87—88°. It has a neutral reaction, gives a dark, cherry-red coloration with ferric chloride, and reduces ammoniacal silver nitrate solution in the cold.

Formamide seems to react with hydroxylamine and sodoacetanilide and benzamide, but only at a higher temperature, and even then very slowly; benzhydroxamic acid was obtained in rhombic plates, melting at 124—125°.

F. S. K.

Intramolecular Change of Allylcarbamides into Isomeric Bases. By S. GABRIEL (*Ber.*, **22**, 2984—2991).—*Propylene-ψ-thiocarbamide*, $CHMe<\begin{matrix}S\cdot C(NH)\\CH_2\cdot NH\end{matrix}>$ is formed when allylthiocarbamide (m. p. 74°; 1 gram) is heated with fuming hydrochloric acid (sp. gr. = 1·17; 3 c.c.) at 100° for an hour, and the clear liquid evaporated on a water-bath. The syrup is treated with 33 per cent. aqueous potash, and extracted with benzene. It has an unpleasant, distinctly basic odour, and when distilled, decomposes with formation of hydrogen sulphide and ammonia. It is soluble in water. The *platino-*

chloride $(C_4H_8N_2S)_2,H_2PtCl_6$, forms orange-yellow crystals; the *aurochloride* crystallises in yellow, indented needles; the picrate melts at 198—200°, and is sparingly soluble. When the base is oxidised by means of hydrobromic acid and bromine-water (Abstr., 1889, 848), *β-methyltaurocarbamic acid*, $SO_3H \cdot CHMe \cdot CH_2 \cdot NH \cdot CO \cdot NH_2$, is formed; this crystallises in colourless crusts, readily soluble in hot water.

β-Methyltaurine, $SO_3H \cdot CHMe \cdot CH_2 \cdot NH_2$, is obtained by heating the acid (5 grams) with crystallised baryta (20 grams) and water (20 c.c.) for five hours at 140—150°. It crystallises in rhombic plates, which swell up when heated.

Propylenethiocarbamide methiodide, $C_4H_6N_2S,MeI$, prepared by evaporating a mixture of the base dissolved in methyl alcohol and methyl iodide, melts at 171—172°.

β-Dimethyltaurine, $SO_3H \cdot CHMe \cdot CH_2 \cdot NHMe$, is obtained by treating the above methiodide with strong potash, and extracting the base with benzene. The base (15 grams) is then dissolved in water (300 c.c.), neutralised with hydrobromic acid, treated with bromine-water (2 litres), and heated on a water-bath, until the oil which separates is redissolved. The whole is evaporated to dryness, dissolved in hot water (15 c.c.), and allowed to cool. Crystals of *dimethyltaurocarbamic acid*, $SO_3H \cdot CHMe \cdot CH_2 \cdot NMe \cdot CO \cdot NH_2$ (about 3 grams) separate; these melt at 230—240°. The filtrate from these crystals is evaporated down, and heated with water (15 c.c.) and baryta (30 grams) at 150—160° for three hours. The product is freed from barium, evaporated to dryness, and dissolved in absolute alcohol (40 c.c.). It is then further purified from the potassium bromide still remaining by means of platinic chloride. It crystallises from 96 per cent. alcohol in flattened prisms, melts at 220—223°, and is extremely soluble in water.

Propylenecarbamide, $CHMe<\begin{matrix}O \cdot C(NH)\\CH_2 \cdot NH\end{matrix}>$ is formed by the oxidation of allylcarbamide. The *picrate* crystallises in long, lustrous needles, melting at 185—186°. N. H. M.

Ethylenelactic Acid. By M. Siegfried (*Ber.*, **22**, 2711—2717).—The mother liquors from the crystalline zinc paralactate, prepared from (horse) flesh, contain, as has been previously shown by Wislicenus (*Annalen*, **167**, 302), small quantities of a zinc salt, which does not crystallise. The author finds that this amorphous zinc salt is a salt of acetyllactic acid. When it is dissolved in alcohol and reprecipitated with ether, it is partially converted into a basic salt, from which acetyllactic acid can be obtained in colourless needles, melting at 166—167°. This formation of zinc acetyllactate is explained by the facts that flesh extract always contains traces of acetic acid, and that acetyllactic acid is produced in small quantities when an aqueous solution of zinc paralactate is boiled with zinc acetate.

Acetyllactic acid, $OAc \cdot CHMe \cdot COOH$, is also formed in small quantities when paralactic acid is repeatedly evaporated with 30 per cent. acetic acid. It can be obtained in somewhat larger quantities by gradually adding finely divided zinc paralactate (1 part) to anhydrous

zinc acetate (4 parts), heated to its melting point, and keeping the mixture in a liquid condition until it forms a homogeneous paste. The melt is digested with hot water, the cold solution treated with dilute sulphuric acid and quickly extracted with pure ether; the resulting syrup dissolved in water, the filtered solution evaporated with glacial acetic acid ($\frac{1}{3}$ vol.), and the crystals which separate are spread on a porous plate. Acetyllactic acid can also be prepared by heating paralactic acid (1 part) with glacial acetic acid (1 part), and sodium acetate ($1\frac{1}{2}$ parts), at 180° for four hours; it is isolated as already described.

The acid prepared by these methods has the same melting point and the same crystalline form as that obtained from flesh extract. It is readily soluble in alcohol and most ordinary solvents, but when kept it becomes insoluble in alcohol, does not melt below 300°, and decomposes at a higher temperature, but without melting; this insoluble modification is only slowly hydrolysed by alkalis, whereas the original acid (m. p. 166—167°) is readily decomposed even by water. The acid prepared synthetically and that obtained from flesh do not rotate the plane of polarisation.

When acetyllactic acid, prepared from paralactic acid, is boiled with soda, it is decomposed into acetic acid and optically inactive lactic acid; the occurrence of the latter in flesh extract, a fact which has been observed by Heintz, may be due to the previous formation of acetyllactic acid.

Lactic acid yields an acetyl-derivative identical with the compound described above in crystalline form, in melting point, and in its behaviour with solvents; the same acetyl-derivative can also be obtained in small quantities by carefully decomposing ethyl acetyllactate with cold water.

F. S. K.

Conversion of Pentamethylene-derivatives into Benzene-, Pyridine-, and Thiophen-derivatives. By A. HANTZSCH (*Ber.*, 22, 2827—2840).—A compound of the composition $C_6H_5Cl_3BrO_2$ is formed when trichloropentenedihydroxycarboxylic acid (1 part) is heated for a few minutes at 100° with bromine (5 parts) and water (5 parts) (compare Abstr., 1889, 853). It crystallises in well-defined, quadratic prisms, melts at 87°, and is readily soluble in alcohol and ether, but rather sparingly in water. It quickly loses 1 mol. H_2O when kept over sulphuric acid, a second molecule of water being very slowly given off under the same conditions. The anhydrous compound can also be obtained by recrystallising the hydrate from hot chloroform, from which it separates in hexagonal prisms melting at 136°. Chlorobromanilic acid is formed when the hydrate is warmed with excess of alkali, but a portion is completely decomposed; this reaction takes place quantitatively when the hydrate is boiled with a concentrated solution of sodium carbonate, the characteristic red crystals of the sodium salt of chlorobromanilic acid separating from the hot solution. The hydrate does not combine with phenylhydrazine, it gives the same decomposition-products as trichloropentenedihydroxycarboxylic acid when heated at 130° with excess of bromine and water, and it is reconverted into the original acid when reduced with a small quantity

of sodium amalgam in alcoholic solution. These facts seem to show that this bromo-compound is a pentene-derivative of constitution analogous to that of trichloropentenedihydroxycarboxylic acid, but the following experiments point to a totally different constitution. It is not acted on by concentrated sulphuric acid with formation of an open-chain ketone acid as is the case with the pentenecarboxylic acid. It has no well-defined acid properties, only a feeble acid reaction, and dissolves in sodium carbonate without evolution of carbonic anhydride, and not more readily than in water. It can be extracted from slightly alkaline solutions with ether, and it cannot be accurately titrated with baryta and phenolphthaleïn. Its electrical conductivity was examined by Ostwald, and found to be seventy times less than that of the original acid, a fact which shows beyond doubt that the two compounds are analogously constituted. The constitution of this bromo-compound is, therefore, most probably

$$C(OH)_2<\begin{matrix}CCl_2-C(OH)_2\\C(OH)_2\cdot CHBr\end{matrix}>CHCl.$$

β-Chloropyridine is formed when a solution of 1·2-chlorodiketopentamethylene is boiled with ammonia or when a solution of the sodium-derivative is boiled with any ammonium salt. The reaction is best carried out by adding ammonium acetate to a warm, saturated solution of the sodium-derivative and heating the mixture to boiling, when chloropyridine distils with the steam. This pyridine-derivative is identical with the β-chloropyridine obtained by Ciamician from chloroform and potassium-pyrroline.

β-Chloropyridine picrate crystallises in slender, yellow needles melting at 135° with previous softening. The *mercurochloride* crystallises in small, colourless needles melting at about 180°. The *aurochloride* forms moss-like needles and decomposes at about 200°.

α-Thiophenaldehyde is produced when 1·2-chlorodiketopentamethylene is treated with hydrogen sulphide at a temperature below 100°, and the reaction takes place almost quantitatively when hydrogen sulphide is passed into a solution of the sodium-derivative heated to 30—40° and finally to boiling; the aldehyde distils with the steam, and only small quantities of resinous products remain. The thiophenaldehyde thus obtained gives all the characteristic colour reactions for this compound, and it is converted into the corresponding acid on exposure to the air. It combines with hydroxylamine, yielding the aldoxime (m. p. 128°), and with phenylhydrazine, forming the hydrazone which melts at 134·5°. F. S. K.

Decomposition-products of Chloranilic Acid. By A. HANTZSCH (*Ber.*, **22**, 2841—2853)—*Tetrachloroketotrihydroxypentamethylenecarboxylic acid*, $\begin{matrix}CO-CCl_2\\C(OH)_2\cdot CCl_2\end{matrix}>C(OH)\cdot COOH$, is produced when chloranilic acid ($\frac{1}{2}$ mol.) or trichlorodiketopentamethylenehydroxycarboxylic acid (1 mol.) is treated with sodium hypochlorite, but the formation takes place slowly and only in neutral solutions (compare Abstr., 1888, 1190). It is best prepared by dropping a solution of sodium hypochlorite into a cold aqueous solution of pure

potassium chloranilate until the colour disappears, then adding a volume of the hypochlorite solution equal to or rather larger than that already employed, and keeping the mixture for 24 hours; it is then treated with concentrated hydrochloric acid, extracted at least four times with ether, and the crude product spread on a porous plate. It crystallises in small, colourless needles, melts and is completely decomposed at 216°, and is very readily soluble in water and alcohol; it generally crystallises with 2 mols. H_2O, both of which it loses slowly when kept over sulphuric acid. It resembles the original trichlorinated acid in appearance and is, like the latter, completely decomposed by alkalis, yielding oxalic acid. It does not combine with orthotoluylenediamine or with phenylhydrazine, and it is very stable towards oxidising agents; it is not acted on by boiling bromine-water, only very slowly by potassium chlorate and hydrochloric acid, and it crystallises unchanged from hot concentrated nitric acid. It is not acted on by hot sulphuric acid, in which it is only very sparingly soluble. It is a bibasic acid, and measurements of its electrical conductivity show that it is a simple chloro-substitution derivative of the trichlorinated acid. The *ammonium* salt, $C_6H_2Cl_4O_6(NH_4)_2 + H_2O$, crystallises in short prisms, melting at 147—148° with decomposition, when an alcoholic solution of the acid is saturated with ammonia and allowed to evaporate in the air. The *barium* salt crystallises well and is very readily soluble in acetic acid and moderately easily in water. The *lead*, *silver*, and *mercuric* salts are amorphous and sparingly soluble, but the *mercurous* salt crystallises well. The acid gives a red coloration with ferric chloride. When the acid is heated with excess of bromine and water at 130°, it is decomposed into carbonic anhydride, oxalic acid, and tetrachlorodibromacetone.

Chlorodiketopentamethylenehydroxycarboxylic acid,

$$\begin{array}{l}\mathrm{CO{\cdot}CHCl} \\ \mid \\ \mathrm{CO-CH_2}\end{array}\!\!>\mathrm{C(OH){\cdot}COOH},$$

is obtained when a well-cooled ammonical solution of the corresponding trichloro-derivative is treated with zinc-dust, in small portions at a time, until there is no further development of heat; the solution is then filtered, acidified, extracted with ether, and the crude acid purified by converting it into the ammonium salt. The yield is small. It crystallises from ether in colourless, microscopic needles, melts at 147° with decomposition, and behaves with solvents like the other acids of this class. The *ammonium* salt, $C_6H_3ClO_5(NH_4)_2$, crystallises from water, in which it is readily soluble, in short, thick prisms, and decomposes at about 140°, but has no well-defined melting point. Solutions of lead, silver, and mercurous salts produce precipitates in neutral solutions of the ammonium salt; when orthotoluylenediamine hydrochloride is added to a warm concentrated solution of the ammonium salt, a yellowish-green *azine* is precipitated and phenylhydrazine acetate precipitates an oily *hydrazone* which gradually solidifies. When the acid is treated with concentrated sulphuric acid, it yields a syrupy acid, probably chlorodiacetylglyoxylic acid, and when warmed with excess of bromine it is decomposed into chloro-

pentabromacetone (m. p. 91—92°), carbonic anhydride, and oxalic acid.

Dichlorodiketopentamethylenehydroxycarboxylic acid can be obtained in like manner from the corresponding tetrachloro-derivative, but the yield is very small; it is a syrup and is decomposed by concentrated soda in the cold, yielding large quantities of oxalic acid.

Tetrachlorodiacetylglyoxylic acid, $COOH\cdot C(OH)_2\cdot CCl_2\cdot CO\cdot CO\cdot CHCl_2$, is obtained when trichlorodiacetylglyoxylic acid (1 mol.) is treated with sodium hypochlorite (1 mol.) as described above. It crystallises in small, colourless needles, melts at 146—147° with decomposition, and is very readily soluble in all ordinary solvents. It forms an *azine* and a crystalline *hydrazone*, and it is readily decomposed by sodium hypochlorite.

Dichloropyruvic acid, $CHCl_2\cdot CO\cdot COOH$, is obtained when tetrachlorodiacetylglyoxylic acid (1 mol.) is treated with sodium hypochlorite (1 mol.) in neutral aqueous solution. It crystallises in needles with $\frac{1}{2}$ mol. H_2O, melts at 78—79°, and loses its water over sulphuric acid; it is very readily soluble in water, but is reprecipitated on adding concentrated hydrochloric acid. It combines with phenylhydrazine forming a *hydrazone* which contains chlorine.

Bromodichloropyruvic acid, $CBrCl_2\cdot CO\cdot COOH$, can be prepared by heating the preceding compound with bromine and water at 120°; it separates from water with 3 mols. H_2O in colourless crystals, loses its water over sulphuric acid, and is immediately decomposed into bromodichloromethane and oxalic acid when treated with cold alkalis.

F. S. K.

Two Isomeric Symmetrical Dimethylglutaric Acids. By N. ZELINSKY (*Ber.*, **22**, 2823—2827).—*Ethyl dimethyldicyanoglutarate*, $CH_2[CMe(CN)\cdot COOEt]_2$, is formed when ethyl sodocyano-α-propionate (2 mols.) is treated with methylene iodide (1 mol.) in alcoholic solution; the yield of the crude product is about 50 per cent. of the theoretical quantity. It boils at 282—288° with only slight decomposition (at 165—170° under 10—12 mm.), but could not be obtained pure. When boiled for 10—12 hours with moderately concentrated hydrochloric acid it yields two isomeric symmetrical dimethylglutaric acids, $CH_2(CHMe\cdot COOH)_2$, which can be separated by fractional crystallisation. The one melts at 102—104°, the other at 128°; the *silver* salts, $C_7H_{10}Ag_2O_4$, of both acids are moderately stable and undergo no change when heated at 100°.

Diphenylglutaric acid (symmetrical) has been prepared by the author and Feldmann, and is at present under investigation.

Dimethyladipic acid (symmetrical) seems to exist in two isomeric modifications.

F. S. K.

Dicarboxylic Acids, $C_8H_{14}O_4$. By K. AUWERS and V. MEYER (*Ber.*, **22**, 3005).—Of the two acids obtained by the action of silver on ethyl α-bromisobutyrate (Abstr., 1889, 1145), the volatile acid is tetramethylsuccinic acid, whilst the non-volatile acid is symmetrical dimethyladipic acid, $C_2H_4(CHMe\cdot COOH)_2$ (compare Zelinsky, pre-

ceding abstract). According to Hell (*Ber.*, **10**, 2229), a portion of the α-bromisobutyric acid decomposes into hydrogen bromide and methylacrylic acid, which unite, according to Fittig and Engelhorn (*Annalen*, **200**, 65), to form β-bromisobutyric acid. The normal product of the action of silver on the latter would be the above dimethyladipic acid. In order to test the correctness of this view, the authors are studying β-bromisobutyric acid and especially its behaviour towards silver. N. H. M.

Allylethylsuccinic Acids. By E. HJELT (*Ber.*, **22**, 2906).—Allylbutenyltricarboxylic acid was heated until the evolution of carbonic anhydride ceased, and the residue was crystallised from boiling water. Two isomeric *allylethylsuccinic acids*, $C_9H_{14}O_4$, were obtained. The *para-acid* crystallises in small, rhombic scales, sparingly soluble (1 : 110) in water, and melts at 155—156°; the *anti-acid* crystallises in small plates, more readily soluble (1 : 37) in water, and melts at 110—115°. L. T. T.

Action of Bromine on Ethyl Oxalacetate. By W. WISLICENUS (*Ber.*, **22**, 2912—2915).—*Ethyl dibromoxalacetate*,

$$COOEt{\cdot}CO{\cdot}CBr_2{\cdot}COOEt,$$

is formed by treating a solution of the acetate in an indifferent solvent with a slight excess of bromine. It forms a colourless, oily liquid which boils at 165—168° under 20 mm. pressure; it is insoluble in water, and gives no coloration with ferric chloride. It is easily decomposed by bases, the resolution taking place between the ketone- and dibromo-groups. Ammonia, for instance, yields oxamide, dibromacetamide, and alcohol; whilst phenylhydrazine yields oxalic diphenylhydrazide $(CO{\cdot}N_2H_2Ph)_2$.

Ethyl monobromoxalacetate, $COOEt{\cdot}CO{\cdot}CHBr{\cdot}COOEt$, is obtained by the action of exactly the theoretical quantity of bromine on pure ethyl oxalacetate in carbon bisulphide solution; its purification is possible by fractional distillation in a vacuum, but is most easily effected by the crystallisation of the sodium-derivative. It is an oil boiling at 144—147° under 8—12 mm. pressure. Its alcoholic solution is coloured intensely red by ferric chloride. Attempts to isolate the acid $COOH{\cdot}CO{\cdot}CH(OH){\cdot}COOH$ by substituting hydroxyl for the bromine proved futile, although this acid seems to be formed, but immediately decomposed again. L. T. T.

Tricarballylic Acid. By W. O. EMERY (*Ber.*, **22**, 2920—2924).—*Tricarballylic chloride*, $C_6H_5Cl_3O_3$, prepared by the action of phosphoric chloride on the acid, forms a thick, pale-yellow oil boiling, with slight decomposition, at 140° under 14 mm. pressure. *Tricarballylanilide*, $C_3H_5(CONHPh)_3$, obtained by the action of aniline on the chloride, crystallises in very thin, white needles melting at 252°. *Trimethyl tricarballylate*, $C_3H_5(COOMe)_3$, is a colourless liquid boiling at 150° under 13 mm. pressure; sp. gr. = 1·18221 at 20° (water at 4° = 1). With concentrated aqueous ammonia, it yields *tricaballyl-*

amide, $C_3H_5(CONH_2)_3$, which crystallises in long prisms easily soluble in water, very sparingly in alcohol, ether, chloroform, &c., and melting with decomposition at 205—207° to a black liquid.

L. T. T.

Phenylthiophen. By A. RENARD (*Compt. rend.*, **109**, 699—700).—When a mixture of the vapours of toluene and sulphur in equal proportions by weight is passed through an iron tube heated to dull redness, the products are hydrogen sulphide, carbon bisulphide, and a blackish substance which solidifies on cooling. If the latter is distilled, it yields some carbon bisulphide and unaltered toluene, and a yellow, solid substance which is purified by repeated crystallisation from alcohol. A portion of the product is only very slightly soluble in alcohol, and consists of another thiophen-derivative.

Phenylthiophen, C_4SH_3Ph, forms brilliant, white plates, which melt at 170°, sublime easily, and boil at about 300°. It is only slightly soluble in cold alcohol, more soluble in boiling alcohol, very soluble in benzene, light petroleum, chloroform, and carbon bisulphide, but less soluble in ether. With isatin and sulphuric acid, it gives a blue coloration, and with phenanthraquinone and sulphuric acid, a green coloration. Chromic acid in presence of acetic acid converts it into benzoic acid.

Dibromophenylthiophen, $C_6H_4Br{\cdot}C_4SH_2Br$, is obtained by the action of excess of bromine, and forms very small, white crystals, which melt at 195°, and are almost insoluble in all ordinary solvents, but dissolve to some extent in carbon bisulphide. It gives a green coloration with phenanthraquinone and sulphuric acid, and, when oxidised, yields parabrombenzoic acid, melting at 251°.

Dinitrophenylthiophen, $C_6H_4NO_2{\cdot}C_4SH_2{\cdot}NO_2$, is obtained by the gradual addition of phenylthiophen to fuming nitric acid. It forms a yellow, non-crystallisable powder which melts at 178°, is almost insoluble in all ordinary solvents, and, when oxidised, yields paranitrobenzoic acid melting at 233°.

Phenylthiophendisulphonic acid is formed by heating phenylthiophen with ordinary sulphuric acid at a temperature of 50° to 60°; it yields a barium salt which is very soluble in water and very difficult to crystallise.

Phenylthiophentetrasulphonic acid is obtained by the action of Nordhausen acid on phenylthiophen; its barium salt is very soluble in water.

C. H. B.

Derivatives of Ethylbenzene. By W. SUIDA (*Ber.*, **22**, 2919—2920).—With regard to Sempotowski's work (this vol., p. 54), the author points out that orthethylphenol and its sulphonic acid have already been described by Suida and Plohn (Abstr., 1881, 268) and others.

L. T. T.

Xylylene Sulphides. By E. HJELT (*Ber.*, **22**, 2904—2905).—Ortho-xylylene sulphide, described by Leser (Abstr., 1884, 1313), crystallises at 0°, but is very unstable, changing quickly into a black

resin. The *mercurochloride*, $(C_8H_8S)_2,HgCl_2$, crystallises in soft, long needles. A *platinochloride* and a *bromide* were also obtained. *Orthoxylylmethylsulphine iodide*, SC_8H_8MeI, forms yellowish crystals melting at 154—155°. When this iodide is treated with water and silver oxide, a strongly basic *sulphonium hydroxide* is formed.

When meta- and para-xylylene sulphides are treated with potassium sulphide, insoluble, white, amorphous compounds are formed. The anthor has not yet obtained them quite pure, but analyses leave little doubt but that they are the corresponding *meta-* and *para-xylylene sulphides*. L. T. T.

Ethereal Oil of Betel-leaves. By J. F. EYKMAN (*Ber.*, **22**, 2736—2754. Compare Bertram and Gildemeister, Abstr., 1889, 863).—The leaves of *Chavica Betle Miq.* when distilled with water, yield a small quantity of a yellowish-green oil which has a burning taste, a peculiar, pleasant smell, and is feebly lævorotatory. When shaken with concentrated potash it is partially dissolved, and on adding sulphuric acid to the solution, a phenol (chavicol) is precipitated. The portion insoluble in alkali can be separated by fractional distillation into two principal portions, boiling at 175—190° and 255—265° respectively.

Chavicol, $C_9H_{10}O$, is a colourless liquid, boils at about 237°, and is soluble in alcohol, ether, chloroform, and light petroleum in all proportions, but only sparingly in water aud ammonia. With ferric chloride, the aqueous solution gives a blne coloratiou, which disappears on adding alcohol. Molecular-weight determinations by Raoult's method, vapour-density determinations carried out in an atmosphere of hydrogen nnder reduced pressure, and an examination of its refractive properties showed that the molecular formula of this phenol is $C_9H_{10}O$. It is a powerful antiseptic, its action on bacteria being five times as strong as that of phenol and about twice as strong as that of eugenol. The *ethyl*-derivative, $C_9H_9{\cdot}OEt$, prepared by heating chavicol with potash and ethyl iodide in alcoholic solution, is a colourless liquid boiling at about 232°; when oxidised with chromic acid, it yields parethoxybenzoic acid (m. p. 195°). Its molecular formula was found to be $C_{11}H_{14}O$, by the same methods as those employed in the case of chavicol. The *methyl*-derivative, $C_9H_9{\cdot}OMe$, prepared in like manner, is a colourless liquid boiling at about 226; its molecular weight, determined optically, was found to be 151. When oxidised with potassium permanganate, it yields anisic acid and an acid of lower melting point, probably paramethoxyphenylacetic acid.

The fraction boiling at 175—190° and insoluble in alkali (see above) probably contains several terpenes, perhaps also cymene and cineole, bnt it is free from pinene; no pure compound could be isolated from the mixture.

The fraction boiling at 255—265° contains a colourless sesquiterpene, $C_{15}H_{24}$, boiling at about 260°.

Chavicol has most probably the constitution $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{:}CH_2$ [= 1 : 4], as is shown by its chemical properties and also by its low refractive power.

An optical examination of isosafrole and isoeugenol showed that both compounds probably contain the propenyl-group—CH:CHMe.

F. S. K.

Safrole. By T. POLECK (*Ber.*, **22**, 2861—2863).—When safrole is oxidised with potassium permanganate, it yields piperonal, piperonylic acid, formic acid, acetic acid, oxalic acid, and carbonic anhydride, but no propionic acid is formed, as stated by Schiff (Abstr., 1884, 1338); this result is in accordance with the view that safrole is the methylene ether of an allyldihydroxybenzene. F. S. K.

Phloroglucinol. By Z. H. SKRAUP (*Monatsh.*, **10**, 721—725).—The author has previously described the action of benzoic chloride on phloroglucinol in presence of alkalis (Abstr., 1889, 1152), and has now, by careful fractional crystallisation of the product from benzene, succeeded in obtaining the following compounds in a state of purity. *Diresorcinyl tetrabenzoate*, $C_{12}H_6O_4Bz_4$, is readily soluble in hot benzene, and crystallises from it on cooling in prisms melting at 199°. *Phloroglucinyl tribenzoate*, $C_6H_3O_3Bz_3$, is insoluble in water, only slightly soluble in alcohol, and crystallises from benzene in plates or scales melting at 173—174°.

Commercial phloroglucinol may best be purified by first converting it by means of potassium hydrogen carbonate into phloroglucinolcarboxylic acid (which may be obtained free from other compounds by taking advantage of the fact that it is soluble with difficulty in a solution of potassium carbonate and alcohol), and afterwards reproducing the phloroglucinol by boiling the pure carboxylic acid with water (compare Will, Abstr., 1885, 906). G. T. M.

Action of Alkalis and Ammonia on Halogen-substituted Quinones. By F. KEHRMANN (*J. pr. Chem.* [2], **40**, 365—375).—Paradiethoxydichloroquinone (Abstr., 1889, 707) melts at 97—98°; it has the same formula as Stenhouse's ethyl chloranilate, obtained by the action of ethyl iodide on silver chloranilate, but is not identical with it. The author distinguishes the former as the β-compound, and the latter as the α-compound. Both are obtained by the action of potassium ethoxide on chloranil, but the β-compound largely predominates when the solution is weak and the temperature low. If the reaction for preparing the β-compound (*loc. cit.*) is allowed to proceed near the boiling point of alcohol, a considerable quantity of the α-compound crystallises with the β-compound, and may be separated from it by fractional crystallisation from hot alcohol, in which the α-compound is more soluble, as small, red needles melting at 104—105°. The α-compound cannot be changed into the β-compound, or *vice versâ*, by crystallisation.

The β- and α-methyl-compounds are also both produced by the action of potassium methoxide on chloranil, the β-compound predominating when the temperature is lower. By crystallisation from benzene, the dimethoxydichloroquinone (β-compound) is separated at first, either as grains or needles, melting at 157—158°, not 130° (*loc. cit.*). The *methyl chloranilate* (α-compound) separates from the mother liquor of the β-compound in leafy crystals melting at

141—142°, and identical with those obtained by the action of methyl iodide on silver chloranilate.

By acting on the α-ethyl-compound with ammonia and with aniline, chloranilamide, and chloranilanilide are obtained respectively; they are identical with the amide and anilide produced by the action of ammonia and aniline on chloranil, and are, therefore, paradiamidoparadichloroquinone [$O_2 : Cl_2 : (NH_2)_2 = 1:4:2:5:3:6$] and paradianilidoparadichloroquinone [$O_2 : Cl_2 : (NHPh)_2 = 1:4:2:5:3:6$] respectively.

When the β-ethyl-compound is heated with excess of aniline in alcohol for some time, it becomes dark-green, and dark-green crystals with a violet iridescence separate. With ammonia instead of aniline, a deep-violet colour is produced, and by diluting the alcoholic solution with water dark violet needles are obtained. When the β-compound is heated with excess of aqueous potash, most of it is converted into potassium chloranilate; but if dilute potash is added, drop by drop, in slight excess to a cold alcoholic solution, the liquid becomes successively violet, yellow-red, and colourless; if now heated it becomes permanently violet, and a violet potassium salt may be crystallised out. These matters are still under investigation.

When the β-compound is shaken with stannous chloride in ethereal solution, the β-quinol only is obtained, but if an acetic acid solution is so treated both the β-quinol and α-quinol are obtained. The α-compound yields only the α-quinol.

α-Diethoxydichloroquinol melts at 151—152°, not 148—150° (*loc. cit.*).

β-Diethoxydichloroquinol forms lustrous, colourless leaves or needles melting at 108—109°; in water they melt at 70°, the greater part dissolving and separating again on cooling.

α-Dimethoxydichloroquinol forms short, colourless prisms melting at 195—196°, soluble in the ordinary solvents except water.

β-Dimethoxydichloroquinol forms colourless prisms melting at 156—157°. A. G. B.

Paratoluidine Oxalate. By E. BORNEMANN (*Ber.*, **22**, 2710).— Paratoluidine oxalate, $C_6H_7NH_2,C_2O_4H_2$, crystallises with $\frac{1}{2}$ mol. of water. F. S. K.

Action of Bromine on Paratoluidine in the Presence of Concentrated Sulphuric Acid. By R. HAFNER (*Ber.*, **22**, 2902—2904; compare this vol., p. 37).—125 grams of bromine was added to a solution of 30 grams of paratoluidine in 400 grams of sulphuric acid, and the whole allowed to remain for 10 days. A good deal of paratoluidine remained unchanged, whilst metabromoparatoluidine and orthobromoparatoluidine were formed. Sulphuric acid, therefore, seems to have a tendency to promote the formation of a meta-derivative, as was noticed (*loc. cit.*), with chlorine-derivatives. L. T. T.

Action of Aluminium Chloride on Dimethylaniline. By H. GIRAUD (*Bull. Soc. Chim.* [3], 1, 691—693).—Aluminium chloride and dimethylaniline combine with development of heat, and yield a

substance which crystallises in long prisms melting at 88°; no reaction, however, obtains when the original compounds are heated in sealed tubes at 250° for 10 hours.

Dimethylaniline, when heated with excess of aluminium chloride in presence of air, yields a base which crystallises from alcohol in small, felted needles melting at 195°, and coloured green by oxidising agents; it is a tetramethylbenzidine, $NMe_2 \cdot C_6H_4 \cdot C_6H_4 \cdot NMe_2$.

From dimethylaniline containing dimethyltoluidine, by similar treatment, a base melting at 90°, coloured blue-violet by oxidising agents, and which appears to be tetramethyldiamidophenylmethane, is obtained. The author is continuing the research. T. G. N.

Condensation of Phenylenediamines with Butaldehydes. By LASSAR-COHN (*Ber.*, **22**, 2724—2726).—A compound, $C_{10}H_{14}N_2$, is formed when orthophenylenediamine (10·8 grams) is mixed with a quantity of alcohol insufficient for complete solution, and then treated with isobutaldehyde (7·2 grams); the mixture is boiled for a short time, and the crystalline compound which separates on cooling is purified by pouring its alcoholic solution into warm water. It sublimes in colourless needles, melts at 233°, and is very readily soluble in alcohol, but almost insoluble in ether. The *hydrochloride*, $C_{10}H_{14}N_2,HCl$, crystallises from water and alcohol, melts at 184°, has not poisonous properties, and forms a golden *platinochloride*, $(C_{10}H_{14}N_2)_2,H_2PtCl_6$.

An isomeric compound is obtained in like manner from isobutaldehyde and metaphenylenediamine; it melts at 216°, and separates from benzene and chloroform in crusts. The *platinochloride* has the composition $(C_{10}H_{14}N_2)_2,H_2PtCl_6$.

Isobutaldehyde and paraphenylenediamine yield an oily base, the *platinochloride* of which has the composition $(C_{10}H_{14}N_2)_2,H_2PtCl_6$, but neither the base nor the hydrochloride could be obtained in crystals.

Normal butaldehyde does not react with orthophenylenediamine in solution in absolute alcohol. F. S. K.

Fluorescent Derivatives of Aromatic Metadiamines. By H. SCHIFF and A. VANNI (*Annalen*, **253**, 319—335; compare Schiff, *Annalen*, **140**, 97, and **159**, 64).—Metatoluylenediamine combines with œnanthaldehyde, yielding a compound of the composition $C_7H_6N_2(C_7H_{14})_2$; if the reaction takes place in the cold, the alcoholic solution of the product is only slightly fluorescent until after the addition of a few drops of hydrochloric acid. When metatoluylenediamine is warmed for a few hours with a slight excess of œnanthaldehyde, an orange, vitreous mass is obtained the alcoholic solution of which is highly fluorescent. This product consists of a portion readily soluble in cold alcohol, probably methyltetrahydrodibutylphenanthroline, and a portion which is only sparingly soluble; they both resemble the original product, are very stable, and are not decomposed by warm hydrochloric acid.

A red compound, probably dibutyloctohydrophenanthroline, is formed when œnanthaldehyde is added to a warm alcoholic solution of metaphenylenediamine hydrochloride, and the solution shows a

green fluorescence; a thick oil remains on evaporation, readily soluble in benzene, but more sparingly in ether, and insoluble in water. The *plutinochloride* seems to have the composition $(C_{20}H_{32}N_2)_2,H_2PtCl_6$.

Acetaldehyde, or paraldehyde, combines with metaphenylenediamine hydrochloride in alcoholic solution forming a red, semi-solid compound the solutions of which are deep-orange and, especially when dilute, show a green fluorescence. On adding ammonia to an aqueous solution of the crude product, the free *base*, probably dimethyltetrahydrophenanthroline, is precipitated in the form of a reddish-brown, unstable powder. The *platinochloride*, $(C_{14}H_{16}N_2)_2,H_2PtCl_6$, is an orange, amorphous compound which dissolves sparingly in alcohol, yielding a highly fluorescent solution. When the base is oxidised with potassium permanganate, it yields an acid, and this, like the base itself, gives considerable quantities of pyridine-derivatives ou distillation.

Metaphenylenediamine and metatoluylenediamine hydrochlorides give analogous compounds (alkyl hydrophenanthroline salts) with other aldehydes of the fatty series.

Salicylolmetaphenylenediamine hydrochloride,

$$C_6H_4(N{:}CH{\cdot}C_6H_4{\cdot}OH)_2,HCl,$$

prepared by treating phenylenediamine hydrochloride with salicylic aldehyde in alcoholic solution, is an orange, crystalline compound. The free *base* is a yellow, flocculent substance soluble in alcohol and hydrochloric acid; it is decomposed by acids or by prolonged boiling with water. The *platinochloride*, $(C_{20}H_{16}O_2N_2)_2,H_2PtCl_6$, is a cinnabar-red powder.

Salicylolmetatoluylenediamine, $C_7H_6(N{:}CH{\cdot}C_6H_4{\cdot}OH)_2$, crystallises from a mixture of alcohol and benzene in long, yellow needles and is readily soluble in ether and benzene but only sparingly in alcohol. It has only feeble basic properties, is soluble in moderately concentrated potash, and is converted into a low-melting acetyl-derivative by acetic acid.

Cuminolmetatoluylenediamine, $C_7H_6(N{:}CH{\cdot}C_6H_4Pr)_2$, is a yellow, crystalline powder, melts at about 99° with decomposition, and is very readily soluble in benzene and ether; it has no basic properties and its solutions do not fluoresce.

Cinnamaldehyde combines with metaphenylenediamine hydrochloride in warm alcoholic solution, yielding an orange, unstable powder, most probably tetrahydrodiphenylphenanthroline hydrochloride. Cinnamaldehyde and metaloluylenediamine hydrochloride, under the same conditions, give a red, microcrystalline salt, the very dilute solutions of which show a feeble fluorescence; the platinochloride is a yellowish-red, crystalline powder soluble in alcohol.

Cinnamolmetatoluylenediamine, $C_7H_6(N{:}CH{\cdot}CH{:}CHPh)_2$, is precipitated as an orange powder when cinnamaldehyde is treated with metatolulenediamine in dilute alcoholic solution; it melted at about 180° but could not be obtained in a pure condition. It combines with bromine (2 mols.) yielding a red, unstable powder.

Amidophenyleneoxamic acid combines with fatty aldehydes in alcoholic hydrochloric acid solution, yielding compounds which show

a slight green fluorescence. When the ammonium salt of this acid is treated with a mixture of furfuraldehyde and aniline hydrochloride, a red dye is formed.

Paraphenylenediamine and orthotoluylenediamine do not give fluorescent condensation-products with aldehydes of the fatty series.

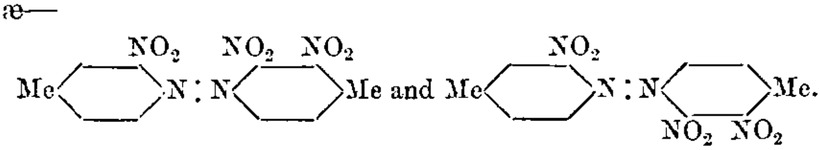
F. S. K.

Azotoluenes and Azoxytoluenes. By J. V. JANOVSKY (*Monatsh.*, **10**, 585—601; compare Abstr., this vol., p. 392 and 865). *Mononitroparazotoluene* is best obtained by heating at 30° a mixture of azotoluene with one-fifth of its weight of nitric acid of sp. gr. 1·43. It may be recrystallised from alcohol, melts at 80°, and has the formula—

$$\overset{3}{NO_2}\cdot C_6H_3\overset{1}{Me}\cdot\overset{4}{N_2}\cdot C_6H_4\overset{1}{Me},$$

since on reduction with tin and hydrochloric acid it yields a mixture of paratoluidine and β-toluylendiamine [$Me : (NH_2)_2 = 1 : 3 : 4$] melting at 88°.

If in the above mentioned operation the temperature is allowed to rise above 30°, or if a stronger acid is used, *dinitroazotoluene* [$Me_2 : (NO_2)_2 : N_2 = 1,1 : 3,3 : 4,4$], melting at 114° is formed. On reduction with alcoholic stannous chloride, this yields β-toluylendiamine and must consequently be regarded as the symmetrical compound. The two trinitroazotoluenes previously described (*loc. cit.*) which melt at 138° and 139° respectively, are both converted on reduction into β-toluylendiamine and the same triamidotoluene [$Me : (NH_3)_3 = 1 : 2 : 3 : 4$], the hydrochloride of which crystallises in scales which become coloured on exposure to the air; they must consequently be regarded as physical isomerides having respectively the formulæ—



G. T. M.

Amidoximes and Azoximes. By F. TIEMANN (*Ber.*, **22**, 2942—2946).—This paper gives a short *résumé* of the work previously done on the subject of diamidoximes and diazoximes by the author and his collaborators.

The oxaleneamidoximes, succineneamidoximes, glutareneamidoximes, isophthaleneamidoximes, and hometerephthaleneamidoximes are soluble in boiling water and alcohol, very sparingly so in ether. Their aqueous solutions show very strongly the characteristic amidoxime reactions. The hydrochlorides of the diamidoximes contain 2 mols. of hydrogen chloride and are highly crystalline, but easily lose a part of the hydrogen chloride. The replacement of the two hydrogens of the two oximide-groups takes place in a normal way, but hitherto all attempts to displace only one of these atoms have proved unavailing. The acid derivatives of the diamidoximes,

$$NO(COR)\colon C(NH_2)\cdot R''\cdot C(NH)\colon NO\cdot COR,$$

pass less easily into the azoximes than the corresponding derivatives

of monamidoximes. The diazoximes so formed have the general formula $<{}^{O-N}_{CR:N}\!\!>C{\cdot}R''{\cdot}C<\!\!{}^{N-O}_{N\cdot CR}>$. The diamidoximes of such dicarboxylic acids as easily form imides decompose very readily into imido-dioximes of the formulæ—

$$\begin{matrix}:C{\cdot}C(N{\cdot}OH)\\ | \\ :C{\cdot}C(N{\cdot}OH)\end{matrix}\!\!>NH, \text{ and } :C<\begin{matrix}C{\cdot}\ddot{C}(N{\cdot}OH)\\ | \\ C{\cdot}\underset{\cdot\cdot}{C}(N{\cdot}OH)\end{matrix}\!\!>NH,$$

thus forming compounds with 5- and 6-atom closed rings which are soluble in water, are sometimes basic, sometimes acid in character, and usually yield stable silver-derivatives.

When hydroxylamine (1 mol.) acts on such dinitriles as yield imidodioximes (1 mol.), basic derivatives are formed isomeric with cyano-amidoximes. The constitution of these compounds is not yet fully proved, but, as an example, that obtained from orthocyanobenzyl cyanide is probably represented by the formula—

$$NH:C<\begin{matrix}C_6H_4{\cdot}CH_2\\ O\text{———}N\end{matrix}\!\!>C{\cdot}NH_2.$$

L. T. T.

Formation of Benzaldoxime. By B. LACHOWICZ (*Ber.*, **22**, 2887—2888).—Benzaldoxime is best prepared by triturating hydrobenzamide (1 mol.) with hydroxylamine hydrochloride; the reaction is at an end in 10 to 15 minutes, and on adding water the benzaldoxime is precipitated as an oil. F. S. K.

Amidoximes and Azoximes. By F. TIEMANN (*Ber.*, **22**, 2758—2761).—The author makes a few general remarks on the papers of Biedermann (this vol., p. 175), Spilker (next abstract), and Miller (this vol., p. 144). F. S. K.

Nitrogen-derivatives of Salicylic Acid. By A. SPILKER (*Ber.*, **22**, 2767—2790).—Salicylamide is best prepared by heating ethyl salicylate at 100° with concentrated ammonia; it melts at 138°.

Dibromosalicylamide, $OH{\cdot}C_6H_2Br_2{\cdot}CONH_2$, prepared by treating a warm, concentrated aqueous solution of the amide with excess of bromine-water, crystallises from dilute alcohol in colourless needles, melts at 183° with decomposition, and is readily soluble in alcohol, ether, and alkalis, more sparingly in benzene and chloroform. In aqueous alcoholic solutions, ferric chloride produces a reddish-violet coloration.

Salicylothiamide, $OH{\cdot}C_6H_4{\cdot}CSNH_2$, is obtained, together with several other compounds, when the amide is melted with phosphorous pentasulphide. It crystallises from hot water in colourless needles, melts at 117—118°, and is readily soluble in alcohol, ether, chloroform, benzene, hot water, and alkalis. It is slowly converted into the amide when boiled with water or alkalis. Ferric chloride in dilute aqueous solutions produces a violet coloration, and a brownish-black precipitate is formed on heating. Lead acetate, copper sulphate, and silver nitrate also produce precipitates in the cold or on warming; these compounds darken in colour with separation of the metal.

Salicylonitrile, $OH{\cdot}C_6H_4{\cdot}CN$, is best prepared by distilling the

thiamide under reduced pressure; it crystallises in colourless needles, melts at 98°, boils at 195° (180 mm.), and is readily soluble in alcohol, ether, benzene, and chloroform, but only sparingly in cold water. With ferric chloride, aqueous solutions give a violet coloration, and with bromine-water a colourless, crystalline precipitate. The compound (m. p. 195°) obtained by Grimaux (*Bull. Soc. Chim.*, **13**, 26) by heating salicylamide with phosphoric anhydride, and also by Ahrens (Abstr., 1888, 266) from orthamidophenol by Sandmeyer's reaction, is not salicylonitrile, although the latter can be obtained by both these methods.

Dibromosalicylthiamide, $OH{\cdot}C_6H_2Br_2{\cdot}CS{\cdot}NH_2$, is obtained when the thiamide is treated with excess of bromine in dilute alcoholic solution; if a solution containing salicylthiamide and salicylamide is gradually treated with bromine-water, monobromosalicylthiamide is precipitated first, the amide remaining in solution. Dibromosalicylthiamide crystallises from alcohol in dark-violet, microscopic needles, melts at about 230° with previous softening, and is moderately easily soluble in alcohol, ether, benzene, and chloroform. yielding violet solutions, but is insoluble in water; it dissolves unchanged in alkalis, forming a dark-violet solution. In alcoholic solutions, silver nitrate, copper sulphate, and lead acetate produce dark-red precipitates.

Salicenylamidoxime, $OH{\cdot}C_6H_4{\cdot}C(NH_2){:}NOH$, prepared by boiling the thiamide with hydroxylamine hydrochloride and sodium carbonate in dilute alcoholic solution, crystallises from water and benzene in thick, colourless needles, melts at 98—99°, and is readily soluble in alcohol, ether, chloroform, acids, and alkalis; in aqueous solutions, ferric chloride produces an intense violet coloration, Fehling's solution and copper sulphate a greenish precipitate, and silver nitrate, on warming, a metallic mirror. The *hydrochloride*, $C_7H_8N_2O_2,HCl$, melts at 175° and is very readily soluble in water. The *platinochloride*,

$$(C_7H_8N_2O_2)_2,H_2PtCl_6,$$

forms small, ill-defined crystals, and is readily soluble in water and alcohol. The *sodium*-derivative, $C_7H_6N_2O_2Na_2$, is precipitated as a colourless, hygroscopic powder when the amidoxime is treated with sodium ethoxide in alcoholic solution and a large volume of ether then added. The compound $C_7H_7N_2O_2Na$ is obtained in like manner when sodium ethoxide (1 mol.) is employed; it is a colourless, crystalline substance and is very hygroscopic. The *copper*-compound has the composition $C_{14}H_{14}N_4O_4Cu$.

Dibromosalicenylamidoxime, $OH{\cdot}C_6H_2Br_2{\cdot}C(NH_2){:}NOH$, prepared from dibromosalicenylthiamide in like manner, crystallises from dilute alcohol in colourless plates, melts at 180°, and is readily soluble in alcohol, ether, acids, and alkalis, but more sparingly in chloroform, benzene, and light petroleum, and very sparingly in water. In alcoholic solutions, copper sulphate produces a greenish precipitate, ferric chloride a reddish-violet coloration; alkaline solutions reduce silver nitrate and give a green precipitate with Fehling's solution. The *copper*-derivative, $(C_7H_5N_2O_2Br_2)_2Cu$, is sparingly soluble in water and alcohol.

Salicenylamidoximesulphonic acid, $SO_3H{\cdot}C_6H_3(OH){\cdot}C(NH_2){:}NOH$, is

obtained when the amidoxime is heated with concentrated sulphuric acid at about 150°: it separates from boiling water in colourless crystals, does not melt below 250°, and is insoluble in alcohol, ether, chloroform, and benzene, and only very sparingly soluble in cold water. The salts of the alkalis and alkaline earths are readily soluble in water. The *barium* salt, $(C_7H_7N_2SO_6)_2Ba$, separates from hot water in colourless, ill-defined crystals.

Benzoylsalicenylamidoxime, $OH{\cdot}C_6H_4{\cdot}C(NH_2){:}NOBz$, crystallises from dilute alcohol in needles, melts at 173°, and is readily soluble in ether, alcohol, chloroform, and benzene, sparingly in alkalis, and insoluble in water and acids. It gives a reddish-violet coloration with ferric chloride and a precipitate with bromine-water. The *acetyl*-derivative, $OH{\cdot}C_6H_4{\cdot}C(NH_2){:}NOAc$, crystallises from warm water in colourless plates, melts at 117°, and is readily soluble in alcohol, ether, alkalis, and acids, but only sparingly in chloroform, benzene, and water; in dilute alcoholic solutions, ferric chloride produces a reddish-violet coloration, and bromine-water a colourless precipitate.

Salicenylbenzenylazoxime, $OH{\cdot}C_6H_4{\cdot}C{<}{}^{NO}_{N}{>}CPh$, prepared by boiling the benzoyl-derivative for a long time with water or heating it alone at 180°, separates from hot dilute alcohol in crystals, melts at 128°, and is readily soluble in alcohol, ether, chloroform, and benzene, but insoluble in water. In dilute alcoholic solutions, copper sulphate produces a green, bromine-water a colourless precipitate, and ferric chloride a violet coloration which quickly disappears. The *ethenylazoxime*, $C_9H_8N_2O_2$, prepared by heating the acetyl-derivative at 125° or by boiling it with water or acetic anhydride, crystallises from dilute alcohol in colourless needles, melts at 77°, and is readily soluble in alcohol, ether, chloroform, benzene, and alkalis, but only sparingly in water. It gives the usual reactions with ferric chloride, copper sulphate, and bromine-water.

Dibenzoylsalicenylamidoxime, $OBz{\cdot}C_6H_4{\cdot}C(NH_2){:}NOBz$, is obtained, together with ethyl benzoate, when the amidoxime is treated with benzoic chloride and sodium ethoxide in alcoholic ethereal solution. It separates from dilute alcohol in colourless, ill-defined crystals, melts at 127°, and is readily soluble in alcohol, ether, benzene, and chloroform, but insoluble in water and acids; it gives a colourless precipitate with bromine-water, and it is decomposed by alkalis. The corresponding *azoxime*, $OBz{\cdot}C_6H_4{\cdot}C{<}{}^{N\cdot O}_{N}{>}CPh$, can be prepared by boiling the dibenzoyl-derivative with water or by heating it above 150°; also by treating salicenylbenzenylazoxime with benzoic chloride and sodium ethoxide in alcoholic solution. It crystallises from alcohol in colourless needles, melts at 120°, and is readily soluble in benzene, ether, and chloroform, but insoluble in water and acids; it is decomposed by warm alkalis, and it gives a colourless precipitate with bromine-water.

Diacetylsalicenylamidoxime, $OAc{\cdot}C_6H_4{\cdot}C(NH_2){:}NOAc$, is formed, together with the corresponding azoxime, when the amidoxime is treated with sodium ethoxide and acetic chloride in ice-cold ethereal

solution, but it cannot be obtained in a pure state. The *azoxime*, $C_{11}H_{10}N_2O_2$, is best prepared by treating sodosalicenylethenylazoxime with acetic chloride in alcoholic ethereal solution. It crystallises from dilute alcohol in colourless needles, melts at 74°, and is very readily soluble in alcohol, ether, chloroform, and light petroleum, but only sparingly in water; it gives a colourless precipitate with bromine-water, and it is quickly decomposed by alkalis.

Salicenylethylamidoxime, $OH\cdot C_6H_4\cdot C(NH_2)\colon NOEt$, is formed, together with its ethyl-derivative, when the amidoxime is heated with sodium ethoxide and ethyl iodide in alcoholic solution. It is a colourless oil, boils at 278° (at 220° under 150 mm.), and is readily soluble in acids and alkalis, but insoluble in water, and only sparingly soluble in light petroleum. In dilute alcoholic solutions, ferric chloride produces a violet coloration, and bromine-water a colourless precipitate. The *ethyl*-derivative, $OEt\cdot C_6H_4\cdot C(NH_2)\colon NOEt$, is a colourless oil, boils at 195° (180 mm.), and is readily soluble in acids, but insoluble in water and alkalis.

Salicenylethylamidoxime chloride, $OH\cdot C_6H_4\cdot CCl\colon NOEt$, prepared by warming the preceding compound with sodium nitrite in dilute hydrochloric acid solution, is a colourless oil, boils at 233—234° (at 178° under about 20 mm.), and is readily soluble in alkalis, but insoluble in water and dilute acids; it gives a reddish-violet coloration with ferric chloride and a colourless precipitate with bromine-water.

Salicenylphenyluramidoxime, $OH\cdot C_6H_4\cdot C(NOH)\cdot NH\cdot CO\cdot NHPh$, prepared by triturating the amidoxime with phenylcarbimide, crystallises from dilute alcohol in colourless plates, melts at 119° with decomposition when heated quickly, and is readily soluble in alcohol, ether, and alkalis, moderately easily in benzene, chloroform, and acids, and insoluble in water; it gives the usual reactions with ferric chloride and bromine-water.

Salicenylethylamidoxime and its ethyl-derivative combine with phenylthiocarbimide, yielding compounds which are insoluble in water and do not crystallise well. Salicenylamidoxime combines energetically with phenylthiocarbimide forming the thiouramidoxime and diphenylthiocarbamide.

Salicenyluramidoxime, $OH\cdot C_6H_4\cdot C(NOH)\cdot NH\cdot CONH_2$, crystallises from dilute alcohol in colourless plates, melts at 148° with decomposition, and is readily soluble in alcohol, benzene, acids, and alkalis, moderately easily in chloroform and ether, and sparingly in water; it gives a reddish-violet or reddish-brown coloration with ferric chloride.

F. S. K.

Anisenyl-, Salicenyl-, and Methylsalicenyl-amidoxime. By J. A. MILLER (*Ber.*, **22**, 2790—2801).—Anisaldoxime melts at 64°; Westenberger (Abstr., 1884, 581) gives 45° as the melting point of this compound. Anisonitrile melts at 61—62°; Henry (*Ber.*, **2**, 667) found the melting point to be 56—57°.

Anisenylamidoxime, $OMe\cdot C_6H_4\cdot C(NH_2)\colon NOH$, is prepared by heating anisonitrile for 6—8 hours at about 90° with hydroxylamine hydrochloride and sodium carbonate in dilute alcoholic solution; the yield is 81 per cent. of the theoretical quantity. It crystallises from

benzene in scales and from hot water in needles, melts at 122—123°, and is readily soluble in alcohol, ether, chloroform, acids, and alkalis, sparingly in hot benzene and hot water, and almost insoluble in light petroleum. The *hydrochloride*, $C_8H_{10}N_2O_2,HCl$, is crystalline, melts at 168° with decomposition, and is soluble in alcohol, but insoluble in ether. The *ethyl*-derivative, $C_{10}H_{14}N_2O_2$, crystallises from dilute alcohol in prisms, melts at 51—52°, and is readily soluble in alcohol, ether, benzene, and chloroform, but insoluble in light petroleum. The *acetyl*-derivative, $C_{10}H_{12}N_2O_3$, crystallises from dilute alcohol in prisms, melts at 106°, and is readily soluble in alcohol and chloroform, but only sparingly in benzene and ether. The *azoxime*, $OMe{\cdot}C_6H_4{\cdot}C{<}{}^{N\cdot O}_{N}{>}CMe$, prepared by heating the acetyl-derivative alone, or with water, or with acetic anhydride, crystallises in colourless needles, melts at 68°, and is readily soluble in alcohol, ether, benzene and chloroform, but more sparingly in light petroleum.

Ethylideneanisenylamidoxime, $OMe{\cdot}C_6H_4{\cdot}C{<}{}^{N\cdot O}_{NH}{>}CHMe$, is obtained by dissolving the amidoxime in aqueous acetaldehyde; it crystallises from alcohol in colourless needles, melts at 127·5°, and is readily soluble in alcohol, ether, benzene, and chloroform, but only sparingly in light petroleum.

Ethyl anisenylamidoximecarboxylate, $OMe{\cdot}C_6H_4{\cdot}C(NH_2){:}NO{\cdot}COOEt$, prepared by treating the amidoxime with ethyl chlorocarbonate in cold chloroform solution, crystallises from dilute alcohol in colourless plates, melts at 119—120°, and is readily soluble in alcohol, but more sparingly in ether and benzene.

Anisenylcarbonylamidoxime, $OMe{\cdot}C_6H_4{\cdot}C{<}{}^{N\cdot O}_{NH}{>}CO$, crystallises from dilute alcohol in colourless scales, melts at 208°, and is readily soluble in alcohol, ether, and chloroform, but only sparingly in benzene and light petroleum.

Benzoylanisenylamidoxime, $C_{15}H_{14}N_2O_3$, separates from dilute alcohol in crystals, melts at 148°, and is readily soluble in alcohol, ether, chloroform, and benzene, but insoluble in light petroleum.

Anisenylbenzenylazoxime, $OMe{\cdot}C_6H_4{\cdot}C{<}{}^{N\cdot O}_{NH}{>}CPh$, prepared by heating the preceding compound alone, or with water, or by dissolving it in concentrated sulphuric acid, crystallises in colourless plates, melts at 102·5, and is readily soluble in alcohol, ether, chloroform, and benzene.

Anisenylpropenylazoxime-ω-carboxylic acid,

$$OMe{\cdot}C_6H_4{\cdot}C{<}{}^{N\cdot O}_{N}{>}C{\cdot}C_2H_4{\cdot}COOH,$$

is obtained when the amidoxime is melted with succinic anhydride; it crystallises from dilute alcohol in yellowish needles, melts at 140—141°, and is readily soluble in alcohol, ether, and chloroform, but only moderately in benzene, and very sparingly in light petroleum.

Salicylonitrile (compare Spilker, preceding abstract) can be pre-

pared by decomposing acetylsalicylonitrile (compare Lach, Abstr., 1884, 1154) with alcohol.

A polymeride of salicylonitrile is formed in considerable quantities when salicylaldoxime is heated with acetic anhydride. This compound crystallises from boiling nitrobenzene in pale yellow needles, melts at 296—299°, and is sparingly soluble in boiling chloroform, benzene, and ether. When melted with potash, it is decomposed into salicylic acid and ammonia, and when heated at 200° with concentrated sulphuric acid, it is decomposed into phenol, ammonia, and carbonic anhydride.

Ethyl salicenylamidoximecarboxylate, $C_{10}H_{12}N_2O_4$, crystallises from dilute alcohol in colourless needles melting at 96°.

Salicenylpropenylazoxime-ω-carboxylic acid,

$$OH\cdot C_6H_4\cdot C{<}{\overset{N\cdot O}{\underset{N}{}}}{>}C\cdot C_2H_4\cdot COOH,$$

separates from a mixture of benzene and light petroleum in small, well-defined crystals, melts at 116—117°, and is readily soluble in alcohol, ether, and chloroform, but more sparingly in benzene.

Methylsalicylonitrile, prepared by treating salicylonitrile with sodium ethoxide and methyl iodide, boils at 255—256°, and is volatile with steam; Ahrens (Abstr., 1888, 266) gives 265—266° as the boiling point of this compound.

Methylsalicenylamidoxime, $OMe\cdot C_6H_4\cdot C(NH_2)\colon NOH$, prepared by digesting the nitrile with hydroxylamine for a long time, crystallises from benzene in needles, melts at 123°, and is readily soluble in alcohol, ether, chloroform, and hot water, but insoluble in light petroleum.

Methylsalicenylbenzenylazoxime, $OMe\cdot C_6H_4\cdot C{<}{\overset{N\cdot O}{\underset{N}{}}}{>}CPh$, melts at 117°, and is readily soluble in chloroform, alcohol, ether, and benzene, but insoluble in light petroleum. F. S. K.

Action of Hydroxylamine on Orthocyanobenzyl Cyanide. By G. EICHELBAUM (*Ber.*, **22**, 2973—2975).—*Homo-orthophthalene-amidimidoxime*, $C_6H_4{<}{\begin{matrix}CH_2\cdot C(NH_2)\\ C(NH)\text{—}O\end{matrix}}{>}N(?)$, is most readily obtained by keeping an alcoholic solution of orthocyanobenzyl cyanide (1 mol.) and hydroxylamine (rather more than 1 mol.) for several days in a place protected from direct sun-light; it is then filtered from the crystals which separate, and evaporated down. It crystallises from water in long needles (with 2 mols. H_2O) melting at 95°; the anhydrous substance melts at 158°, is very readily soluble in alcohol, insoluble in ether, chloroform, and benzene, &c. It has the same percentage composition as orthocyanophenylethenylamidoxime. but cannot be an amidoxime, as it has only basic properties, and thus resembles the compound obtained by Beidermann from trimethylene dicyanide and hydroxylamine (this vol., p. 126). The *hydrochloride*, $C_9H_9N_3O,HCl$, crystallises in small, lustrous, yellow crystals, is sparingly soluble in water, almost insoluble in alcohol. The *picrate*, $C_9H_9N_3O,C_6H_3N_3O_7$, forms reddish-yellow needles rather more readily

soluble in alcohol than in water, and explodes slightly when the dry substance is heated. When the base is dissolved in dilute hydrochloric acid and treated with sodium nitrite, homo-orthophthalic acid is formed.

N. H. M.

Isophthalenediamidoxime. By G. GOLDBERG (*Ber.*, **22**, 2976—2977).—Metadicyanobenzene is prepared by distilling an intimate mixture (15 to 20 grams) of potassium benzenemetadisulphonate with pure potassium cyanide under diminished pressure. It is first resublimed and then crystallised from alcohol, from which it separates in slender needles melting at 158—159°.

Isophthalenediamidoxime, $C_6H_4[C(NH_2):N\cdot OH]_2$ [= 1 : 3], is formed when metadicyanobenzene (1 mol.), dissolved in benzene, is digested with hydroxylamine (rather more than 2 mols.) in closed flasks at 90°. It crystallises from alcohol in colourless prisms, melts at 193° with decomposition, dissolves readily in hot water and alcohol, sparingly in ether, and shows the characteristic properties of the amidoximes. The crystals contain water of crystallisation (probably $\frac{1}{2}$ mol.), which they lose when exposed to air. The *hydrochloride* is crystalline.

N. H. M.

Homoterephthalenediamidoxime and its Derivatives. By E. ROSENTHAL (*Ber.*, **22**, 2977—2984).—*Homoterephthalenediamidoxime*, $OH\cdot N:C(NH_2)\cdot C_6H_4\cdot CH_2\cdot C(NH_2)N\cdot OH$ [= 4 : 1], prepared by keeping a mixture of hydroxylamine hydrochloride (3 mols.) with the necessary amount of sodium carbonate and paracyanobenzyl cyanide dissolved in alcohol for some days in a closed flask, crystallises from hot water in microscopic prisms, melts at 192° with decomposition, is rather readily soluble in methyl alcohol and acetone, very sparingly in ethyl and amyl alcohols, and is insoluble in ether, benzene, and light petroleum. It shows all the characteristic reactions of the amidoximes. The *hydrochloride*, $C_9H_{12}N_4O_2.2HCl$, dissolves very readily in water, but is not hygroscopic, and is also soluble in alcohol and glacial acetic acid. The *diacetyl-derivative*, $C_{13}H_{16}N_4O_4$, crystallises in groups of needles, melts at 161·5—162°, is soluble in hot water, alcohol, ether, and benzene, and in acids, but not in alcohol; when boiled with water for some hours, it is quantitatively converted into *homoterephthalenediazoximediethenyl*, $CMe\lessgtr^{O\cdot N}_{N—}\gtrless C\cdot C_6H_4\cdot CH_2\cdot C\lessgtr^{N\cdot O}_{—N}\gtrless CMe$. The latter melts at 111·5°, is soluble in hot water, methyl, ethyl, and amyl alcohols, ether, and benzene, &c., and is insoluble in mineral acids. The *dibenzoyl-compound*, $C_{23}H_{20}N_4O_4$, crystallises from hot methyl alcohol, melts at 184°, dissolves in acetone, ethyl acetate, amyl alcohol, and in acids, very sparingly in ethyl alcohol, and is insoluble in water, benzene, and ether. When heated at 150° for four hours, it is converted into *homoterephthalenediazoxime dibenzenyl*, $C_{23}H_{16}N_4O_2$. This forms long, white, matted needles, melts at 179·5°, and is soluble in alcohol, ether, chloroform, and benzene.

Paracyanophenylethenylamidoxime, $CN\cdot C_6H_4\cdot CH_2\cdot C(NH_2):N\cdot OH$, prepared by the action of hydroxylamine (1 mol.) on paracyanobenzyl cyanide (1 mol.), melts at 168°. It is converted by nitrous

acid into paracyanophenylacetamide (m. p., 196°, Mellinghoff, *Inaug. Diss. Berlin*, 1889). The *benzoyl-derivative*,

$$CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}C(NH_2){:}N{\cdot}OBz,$$

forms small, white needles, melts at 171·5—172°, dissolves in methyl and ethyl alcohols, and glacial acetic acid, less readily in benzene and chloroform; it is also dissolved by acids. When heated with water for six hours, it is converted into *paracyanophenylethenylazoximebenzenyl*, $CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}C{\lessdot}\genfrac{}{}{0pt}{}{N{\cdot}O}{N}{\gtrdot}CPh$, which melts at 105°, and is soluble in alcohol, ether, benzene, and chloroform. N. H. M.

Hydrazines. By M. FREUND (*Ber.*, **22**, 2727).—The author replies to the statements of Willgerodt (this vol., p. 40).

Orthonitrophenylhydrazine. By A. BISCHLER (*Ber.*, **22**, 2801—2809; compare Abstr., 1889, 501).—Orthonitrophenylhydrazine, $NO_2{\cdot}C_6H_4{\cdot}N_2H_3$, is best prepared by dissolving orthonitraniline (10 grams) in warm, concentrated hydrochloric acid (100 grams), adding to the well cooled solution an aqueous solution (35 grams) of sodium nitrite (5 grams), and keeping the mixture at the ordinary temperature, with frequent stirring until the crystals of the nitraniline hydrochloride have disappeared; a solution of stannous chloride (32 grams) in concentrated hydrochloric acid (32 grams) is then gradually added, care being taken that the temperature does not rise much above 0°, and the stannochloride which separates from the solution is recrystallised from hot water. The *hydrochloride*, $C_6H_7N_3O_2,HCl$, obtained by decomposing the stannochloride with hydrogen sulphide, crystallises in small, yellow plates or in long, slender needles, is readily soluble in warm alcohol and warm water, but only sparingly in the cold solvents, and is insoluble in ether, benzene, and concentrated hydrochloric acid; it reduces Fehling's solution in the cold, but ammoniacal silver nitrate solution only on warming. The yield of this salt is about 75 per cent. of the theoretical quantity. The free *base* is obtained by treating a hot aqueous solution of the hydrochloride with sodium acetate; it crystallises from benzene in long, cinnabar-red needles, melts at 90°, and is readily soluble in warm alcohol, benzene, and hot water, but only sparingly in ether and light petroleum. The *sulphate*, $(C_6H_7N_3O_2)_2,H_2SO_4$, crystallises in small, pinkish needles, and is readily soluble in hot alcohol, warm water, and dilute sulphuric acid, but insoluble in ether and benzene.

Benzylideneorthonitrophenylhydrazine, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}N{:}CHPh$, separates as a reddish-brown precipitate when benzaldehyde is added to an alcoholic solution of the hydrazine; it crystallises from boiling benzene in dark-red plates, melts at 186—187°, and is moderately easily soluble in hot benzene, but very sparingly in hot alcohol and ether, and insoluble in water. The *formyl*-derivative,

$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH{\cdot}CHO,$$

separates in long, pale yellow needles when the hydrochloride is

heated at 100° with sodium formate and formic acid for about an hour; it crystallises from alcohol, melts at 177°, and is readily soluble in hot water and boiling alcohol, but only sparingly in ether and benzene. Solutions of the formyl-, acetyl-, and benzoyl-derivatives give a red or bluish-violet coloration with alkalis. The *acetyl*-derivative, $NO_2\cdot C_6H_4\cdot NH\cdot NHAc$, prepared by heating the hydrochloride of the hydrazine with sodium acetate and glacial acetic acid, crystallises from alcohol in lemon-yellow needles, melts at 140—141°, and is readily soluble in hot benzene, alcohol, and water. The *diacetyl*-derivative, $NO_2\cdot C_6H_4\cdot NAc\cdot NHAc$, prepared by heating the hydrochloride with sodium acetate and acetic anhydride, crystallises from dilute alcohol in reddish prisms, melts at 57—58°, and is readily soluble in hot water, benzene, alcohol, and cold glacial acetic acid, but only sparingly in hot ether. The *benzoyl*-derivative,

$$NO_2\cdot C_6H_4\cdot NH\cdot NHBz,$$

crystallises from alcohol in pale-yellow needles, melts at 166°, and is readily soluble in ether, benzene, and hot alcohol, but insoluble in water. The *oxalyl*-derivative, $C_2O_2(N_2H_2\cdot C_6H_4\cdot NO_2)_2$, prepared by heating the hydrazine with ethyl oxalate, crystallises from hot aniline and nitrobenzene in small, yellow needles, and is only sparingly soluble in most ordinary solvents.

α-Phenotriazine, $C_6H_4<\begin{matrix}N\cdot CH\\ | \quad \| \\ N\cdot N\end{matrix}$, is obtained, together with dihydrophenotriazine and orthophenylenediamine, when orthonitrophenylhydrazine is reduced with sodium amalgam in dilute acetic acid solution, care being taken that the temperature does not rise much above 30°. The solution is decanted from the mercury, evaporated at a moderate temperature, the residue dissolved in water, and mixed with excess of soda; it is then treated with potassium ferricyanide in the cold until the violet colour changes to yellowish-red, mixed with a large volume of concentrated soda, and extracted three or four times with ether. When the crude product is fractionated, it is separated into a portion boiling at 235—245°, and a portion boiling above 360° which consists of phenylethenylamidine.

Phenotriazine crystallises from benzene in deep-yellow needles, melts at 65—66°, boils at 235—240°, and is volatile with steam. It is readily soluble in alcohol, benzene, warm ether, and warm water, but it separates from the aqueous solution on adding concentrated alkalis; it has a peculiar alkaloïd-like odour, and is a feeble base, the salts being readily soluble in water and alcohol.

α-Phenomethyltriazine, $C_6H_4<\begin{matrix}N\cdot CMe\\ | \quad \| \\ N\cdot N\end{matrix}$, is formed, together with the dihydro-derivative, acetamide, acetamidophenylhydrazine, and phenylenediamine when acetylnitrophenylhydrazine is reduced with sodium amalgam in acetic acid solution; the solution is filtered from small quantities of acetylamidophenylhydrazine, and the triazine is isolated as described above. It melts at 88—90°, boils at 250—255° with slight decomposition, is readily soluble in alcohol, ether, and benzene, and moderately easily in cold water, but only sparingly in light

petroleum; its alkaline solutions oxidise quickly on exposure to the air.

Orthacetylamidophenylhydrazine, $NH_2\cdot C_6H_4\cdot NH\cdot NHAc$ (see above), crystallises from benzene in colourless needles, and melts at 162°.

F. S. K.

Metanitrophenylhydrazine and Parabromorthonitrophenylhydrazine. By A. BISCHLER and S. BRODSKY (*Ber.*, **22**, 2809—2818).—*Metanitrophenylhydrazine hydrochloride*, $NO_2\cdot C_6H_4\cdot N_2H_3,HCl$, is prepared from metanitraniline exactly as described in the case of the corresponding ortho-compound (compare preceding abstract). The yield is 50—60 per cent. of the theoretical. It crystallises in yellowish plates, and is readily soluble in warm alcohol and water, but only sparingly in warm, concentrated hydrochloric acid; it reduces Fehling's solution in the cold, and ammoniacal silver nitrate and platinic chloride on warming. The free *base*, $NO_2\cdot C_6H_4\cdot N_2H_3$, crystallises from alcohol in slender, yellow needles, melts at 93°, and is readily soluble in glacial acetic acid, chloroform, warm benzene, and alcohol, but only sparingly in boiling water. The *sulphate*, $(C_6H_7N_3O_2)_2,H_2SO_4$, separates from hot water in yellow crystals, and is readily soluble in hot water and glacial acetic acid, but only sparingly in boiling alcohol, and insoluble in ether and benzene. The *acetyl*-derivative, $NO_2\cdot C_6H_4\cdot NH\cdot NHAc$, crystallises in golden plates, melts at 145°, and is readily soluble in alcohol, ether, glacial acetic acid, and boiling water, but only moderately easily in benzene. The *diacetyl*-derivative, $NO_2\cdot C_6H_4\cdot NAc\cdot NHAc$, forms brownish plates, melts at 150°, and is readily soluble in the ordinary solvents. The *benzoyl*-derivative, $NO_2\cdot C_6H_4\cdot NH\cdot NHBz$, crystallises from dilute alcohol in yellow, prismatic needles, melts at 151°, and is readily soluble in alcohol, ether, glacial acetic acid, and hot benzene, but insoluble in water. The *dibenzoyl*-derivative, $NO_2\cdot C_6H_4\cdot NBz\cdot NHBz$, crystallises from acetic acid in yellow plates, melts at 153°, and is readily soluble in hot alcohol and benzene, but insoluble in water.

α-Acetyl-β-benzoylmetanitrophenylhydrazine, $NO_2\cdot C_6H_4\cdot NBz\cdot NHAc$, prepared by heating the acetyl-derivative with benzoic anhydride at 160°, separates from cumene in crystalline aggregates, melts at 137°, and is readily soluble in alcohol and glacial acetic acid, but insoluble in benzene.

α-Benzoyl-β-acetylmetanitrophenylhydrazine, $NO_2\cdot C_6H_4\cdot NAc\cdot NHBz$, obtained by heating the benzoyl-derivative with acetic anhydride and sodium acetate, separates from cumene in yellowish, crystalline aggregates, melts at 147°, and sublimes at 100° in small, iridescent needles; it is readily soluble in boiling benzene, alcohol, and glacial acetic acid, and more readily in hot cumene than the preceding compound.

Ethylidenemetanitrophenylhydrazine, $NO_2\cdot C_6H_4\cdot NH\cdot N{:}CHMe$, prepared by warming the hydrazine with acetaldehyde, separates from alcohol in yellow crystals, melts at 98°, and is readily soluble in alcohol, benzene, and ether, but only sparingly in hot water.

Benzylidenemetanitrophenylhydrazine, $NO_2\cdot C_6H_4\cdot NH\cdot N{:}CHPh$, crystallises from boiling alcohol in small, carmine-red needles, melts at 117—118°, and is sparingly soluble in hot alcohol, but readily in ether, hot glacial acetic acid, and benzene.

Acetonenitrophenylhydrazine, $NO_2\cdot C_6H_4\cdot NH\cdot N:CMe_2$, crystallises from dilute alcohol in dark-red needles, melts at 112°, and is readily soluble in warm alcohol, ether, benzene, and glacial acetic acid, but only sparingly in hot water.

Acetophenonenitrophenylhydrazine, $NO_2\cdot C_6H_4\cdot NH\cdot N:CMePh$, crystallises from benzene, melts at 160°, and is only sparingly soluble in hot alcohol, but more readily in benzene and ether.

Benzilmetanitrophenylhydrazine crystallises from benzene in small, orange-yellow needles, melts at 158°, and is readily soluble in warm benzene, but only sparingly in hot alcohol and ether.

Metanitrophenylizinedihydroxytartaric acid separates in crystals when sodium dihydroxytartrate (1 mol.) is treated with hydrochloric acid (1 mol.) and nitrophenylhydrazine hydrochloride in aqueous solution; it melts at 175° with decomposition. *Metanitrodiphenylizinedihydroxytartaric acid*, prepared in like manner but employing 2 mols. of the hydrazine, is a yellow, micro-crystalline powder, melting at about 200°. The last two compounds are only sparingly soluble in hot water, alcohol, benzene, and glacial acetic acid.

The compound, $NO_2\cdot C_6H_4\cdot NH\cdot N:CMe\cdot CH_2\cdot COOEt$, is formed when the hydrazine is treated with ethyl acetoacetate in alcoholic solution; it crystallises from dilute alcohol in yellowish-red plates, melts at 117°, and is sparingly soluble in hot water, but readily in other warm solvents.

Metanitrodiphenylthiosemicarbazide, $NO_2\cdot C_6H_4\cdot NH\cdot NH\cdot CS\cdot NHPh$, prepared by warming the hydrazine (1 mol.) with phenylthiocarbimide (1 mol.) in alcoholic solution, is a dark-yellow, crystalline compound, melts at 146—147°, and is readily soluble in hot alcohol, but only sparingly in benzene and glacial acetic acid.

Diacetylamidophenylhydrazine, $NHAc\cdot C_6H_4\cdot NH\cdot NHAc$, is obtained when acetylnitrophenylhydrazine is reduced with sodium amalgam in acid alcoholic solution, and the crude product boiled with glacial acetic acid; it crystallises from acetic acid in small, dark-yellow needles, melting at 150—151°.

Attempts to prepare paranitrophenylhydrazine were unsuccessful.

Parabromorthonitrophenylhydrazine, $NO_2\cdot C_6H_3Br\cdot N_2H_3$, prepared by the method described in the case of orthonitrophenylhydrazine (compare preceding abstract), separates from benzene in dark-red crystals, melts at 130°, and is readily soluble in alcohol, ether, hot glacial acetic acid, and benzene, but only sparingly in hot water; it reduces silver and platinum salts. The *hydrochloride*, $C_6H_6BrN_3O_2,HCl$, crystallises from water in small, yellowish-red needles. The *sulphate*, $(C_6H_6BrN_3O_2)_2,H_2SO_4$, is a reddish, microcrystalline powder, sparingly soluble in cold alcohol and benzene, but readily in hot alcohol, water, and glacial acetic acid. The *formyl*-derivative,

$$NO_2:C_6H_3Br\cdot NH\cdot NH\cdot CHO,$$

crystallises from alcohol in slender, pale yellow needles, melts at 191°, and is readily soluble in hot alcohol and benzene. The *acetyl*-derivative, $NO_2\cdot C_6H_3Br\cdot NH\cdot NHAc$, crystallises from glacial acetic acid in small, lemon-yellow needles, and is readily soluble in hot benzene, glacial acetic acid, and alcohol, but only sparingly in the

cold solvents. The *benzoyl*-derivative, $NO_2 \cdot C_6H_3Br \cdot NH \cdot NHBz$, crystallises from alcohol in large, yellow plates, melts at 185°, and is readily soluble in hot alcohol, ether, and benzene, but only sparingly in the cold solvents. The *benzylidene*-derivative,

$$NO_2 \cdot C_6H_3Br \cdot NH \cdot N{:}CHPh,$$

crystallises from alcohol in red needles, melting at 207°. The *acetophenone*-derivative, $NO_2 \cdot C_6H_3Br \cdot NH \cdot N{:}CMePh$, crystallises in red needles and melts at 148°.

Parabromorthonitrodiphenylthiosemicarbazide,

$$NO_2 \cdot C_6H_3Br \cdot NH \cdot NH \cdot CS \cdot NHPh,$$

is a yellow, microcrystalline compound, melts at about 160—164°, and is readily soluble in hot alcohol and glacial acetic acid, but only sparingly in ether and benzene.

Parabrom-α-phenotriazine, $C_6H_3Br<\begin{matrix} N \cdot CH \\ | \quad \| \\ N \cdot N \end{matrix}$, is formed when formylparabromorthonitrophenylhydrazine is reduced with sodium amalgam and glacial acetic acid in well-cooled alcoholic solution; the solution is evaporated, the residue dissolved in water, treated with potassium ferricyanide, and the filtered solution mixed with excess of alkali. It crystallises from boiling water in slender, yellow needles, and is readily soluble in hot water and other ordinary solvents, but insoluble in alkalis.

Parabrom-α-phenomethyltriazine, $C_6H_3Br<\begin{matrix} N \cdot CMe \\ | \quad \| \\ N \cdot N \end{matrix}$, prepared from the acetyl-derivative of the hydrazine in like manner, crystallises from water in golden plates, melts at 115°, and is readily soluble in ether, benzene, alcohol, and glacial acetic acid, but only sparingly in cold water.

F. S. K.

Formation of Phenylhydrazides. By E. FISCHER and F. PASSMORE (*Ber.*, **22**, 2728—2736).—The hydroxy-acids of the sugar-group combine very readily with phenylhydrazine in aqueous solution, yielding crystalline hydrazides, which are only sparingly soluble in cold water, can be easily purified, and are readily reconverted into the acid when boiled with baryta. The hydrazides are prepared by treating a moderately dilute (about 10 per cent.) solution of the acid or lactone with a fair excess of phenylhydrazine and an equal quantity of 50 per cent. acetic acid, heating the mixture for from 30 minutes to two hours on the water-bath; the product sometimes crystallises from the hot solution, but generally the separation occurs only on cooling.

The hydrazides of the monobasic hydroxy-acids are all moderately easily soluble in hot water, but the double hydrazides of the polybasic acids are only sparingly soluble.

If the solution contains free mineral acids, it must previously be neutralised with soda or sodium carbonate, and if large quantities of hydrochloric, hydrobromic, or sulphuric acid are present, the acid is

best removed with lead acetate, or baryta, otherwise rather sparingly soluble salts are formed; if the solution contains sugar, the osazone, which is also formed in the reaction, can generally be separated from the hydrazide by crystallisation from hot water.

The hydrazides are, as a rule, easily obtained in a pure condition, and may serve as a means of determining the formula of the acid, but they resemble each other so closely in physical properties that they cannot be suitably employed for purposes of identification. The hydrazides of gluconic acid, galactonic acid, and arabinosecarboxylic acid, for example, cannot be distinguished with certainty; in such cases it is necessary to reconvert the hydrazide into the acid. For this purpose the hydrazide is boiled for half-an-hour with 10 per cent. baryta-water (30 vols.), the phenylhydrazine is extracted with ether, and the residual solution, together with any precipitate which has been produced, is heated to boiling, and the barium precipitated with the requisite quantity of sulphuric acid; on evaporation, the filtered solution yields the free acid or lactone.

All the monobasic acids of the sugar-group, under the conditions described above, give crystalline hydrazides which are sparingly soluble in cold, but moderately easily in hot water. Under the same conditions, saccharic acid, mucic acid, and metasaccharic acid yield hydrazides which are almost insoluble. Glycollic, lactic, and glyceric acids gave negative results, and the limit of the difference in behaviour probably lies between erythroglucic acid and arabonic acid. Formic acid, succinic acid, malic acid, tartaric acid, and many aromatic acids, for example cinnamic acid and gallic acid, yield hydrazides under the conditions described above, but malonic acid forms only an acid hydrazide. The readiness with which the hydrazide formation takes place is evidently dependent on the electronegative character of the acid; if the latter reaches a certain limit, the hydrazide formation takes place in dilute aqueous solution at temperatures below 100°, but, if the acid is less negative in character, the temperature must be raised; in such cases the presence of water does not affect the reaction. If, for example, a dilute aqueous solution of phenylhydrazine acetate is heated for several hours at 130°, a considerable quantity of acetylphenylhydrazine separates from the solution on cooling. Benzoic acid, glyceric acid, and lactic acid are converted into the corresponding hydrazides under the same conditions, but the products do not crystallise readily. At high temperatures, the yield is not quantitative, as the hydrazide is partially decomposed by the water.

The hydrazides can be readily distinguished from the hydrazones, as they all give a reddish-violet coloration with concentrated sulphuric acid and a drop of ferric chloride, a reaction first observed by Bülow (Abstr., 1887, 138); they are, moreover, readily decomposed by alkalis and baryta. They are all colourless, and generally melt, not quite constantly, with considerable evolution of gas.

Gluconic acid phenylhydrazide, $C_6H_{11}O_6 \cdot N_2H_2Ph$, can be prepared by heating gluconic acid (1 part) on the water-bath for 45 minutes with water (10 parts), phenylhydrazine (1 part), and 50 per cent. acetic acid (1 part); it separates from the cold solution in crystals,

and if the mother liquors are heated again for three hours, a further crop of crystals is obtained. The total yield is 81 per cent. of the theoretical. It crystallises in small prisms, softens at about 195°, and melts completely at 200° with decomposition. It is almost insoluble in ether, and only very sparingly soluble in cold water and hot alcohol, but readily in hot water. It can be easily converted into crystalline calcium gluconate by boiling it with baryta as described above, and treating the acid with calcium carbonate; the yield is 85 per cent. of the theoretical.

Galactonic acid phenylhydrazide, $C_6H_{11}O_6\cdot N_2H_2Ph$, can be obtained in like manner from crude galactonic acid; it crystallises in plates, melts at 200—205° when quickly heated, and is moderately easily soluble in hot water, but only sparingly in cold water and hot alcohol.

Arabinosecarboxylic acid phenylhydrazide, $C_6H_{11}O_6\cdot N_2H_2Ph$, prepared from the free acid or the lactone in like manner, melts at 214—216° with decomposition, and resembles the preceding compound.

Dextrosecarboxylic acid phenylhydrazide, $C_7H_{13}O_7\cdot N_2H_2Ph$, obtained from the lactone, crystallises in prisms, melts and is slowly decomposed at 171—172°, and is readily soluble in hot water, but much more sparingly in alcohol.

Mannosecarboxylic acid phenylhydrazide, $C_7H_{13}O_7\cdot N_2H_2Ph$, crystallises from hot water in small prisms; when quickly heated, it melts at 220—223° with decomposition, and is more sparingly soluble than the other hydrazides.

Rhamnosecarboxylic acid phenylhydrazide, $C_7H_{13}O_6\cdot N_2H_2Ph$, crystallises from hot water in small, hexagonal plates, melting at 210° with decomposition.

Saccharinic acid phenylhydrazide, $C_6H_{11}O_5\cdot N_2H_2Ph$, prepared from the lactone, crystallises from hot alcohol in very slender needles, melts at 164—165° with decomposition, and is much more readily soluble in water and alcohol than the preceding compounds.

Formic acid seems to be the only fatty acid which forms a hydrazide in aqueous solution, but even in this case the reaction does not take place quantitatively, as it is accompanied by a slight evolution of gas.

The hydrazides of succinic acid, malic acid, and tartaric acid are formed at 100° in 10 per cent. aqueous solution, but the reactions take place only slowly.

Succinylphenylhydrazine melts at 217—218°; Freund and Goldsmith give 208—209° as the melting point. Malic acid diphenylhydrazide melts, not quite constantly, at 220—223° with decomposition; Bülow found the melting point to be 213°. Tartaric acid diphenylhydrazide melts at about 240° when quickly heated, whereas Bülow gives 226° as its melting point.

Allyltricarboxylic acid and citric acid yield sparingly soluble hydrazides under the conditions described above.

The phenylhydrazine salt of phenylhydrazidemalonic acid separates in crystals when malonic acid (1 part) is heated with phenylhydrazine (3 parts), dilute acetic acid (3 parts), and water (10 parts) for two hours on the water-bath; it separates from hot alcohol or hot

water in crystals, melts at 141—143° with decomposition, and has the composition $C_{15}H_{16}N_4O_3$.

Malonic acid phenylhydrazide, $COOH{\cdot}CH_2{\cdot}CO{\cdot}N_2H_2Ph$, is obtained when the mother liquors from the preceding compound are acidified with sulphuric acid and extracted with ether. It crystallises in colourless needles, melting at 154° with decomposition, is moderately soluble in water, and gives the hydrazide reaction; it reduces Fehling's solution when warmed therewith, and has a strongly acid reaction.

Malonylphenylhydrazine, $CH_2{<}{}^{CO}_{CO}{>}N_2HPh$, is formed, together with water and phenylhydrazine, when the phenylhydrazine salt of the preceding compound is heated at 200° for 15 minutes; it crystallises from hot water in slender, colourless needles, melts at 128°, and is readily soluble in alcohol.

Neither benzoic acid nor phenylhydroxyacetic acid yields a hydrazide when heated with phenylhydrazine in 10 per cent. aqueous solution; cinnamic acid, on the other hand, forms the hydrazide previously described by Knorr (Abstr., 1887, 665), but the yield is not particularly good.

Gallic acid phenylhydrazide, $C_{13}H_{12}N_2O_4$, crystallises from hot water in long prisms, melts at about 187° with decomposition, and is moderately easily soluble in alcohol and hot water.

Gluconic acid anilide, $C_6H_{11}O_6{\cdot}NHPh$, prepared by heating gluconic acid (5 grams) for four hours at 100° with aniline (5 grams), water (50 grams), and acetic acid sufficient for solution, separates from alcohol in crystals, melts at 171°, and is readily soluble in cold water.

The formation of the anilides does not take place as readily as that of the hydrazides, and the products are much more readily soluble in water. F. S. K.

Action of Phenylhydrazine on α-Hydroxy-acids and their Ethyl Salts. By A. Reissert and W. Kayser (*Ber.*, **22**, 2924—2929).—The authors have obtained phenylhydrazidopropionic acid (Abstr., 1884, 1152) by the action of phenylhydrazine on ethyl lactate, and hydrolysis of the ether formed. When equal molecular proportions of phenylhydrazine and α-hydroxybutyric acid are heated together at 150—160°, *pseudophenylhydrazido-α-hydroxybutyric acid*, $C_{10}H_{14}N_2O_2$, is formed. This compound is easily soluble in alcohol, sparingly in ether, crystallises in needles, and melts at 151—152°. It dissolves in boiling acids and alkalis, but is reprecipitated unchanged on cooling. When dissolved in concentrated sulphuric acid, it gives a violet-red coloration. Boiling alkalis do not decompose it, and it is very stable towards reducing agents; it is decomposed by boiling concentrated hydrochloric acid, but besides phenol no decomposition-products could be isolated. These characteristics seem to show that this compound is not a normal hydrazide. With sulphuric acid and potassium nitrite, *nitrosopseudohydrazido-α-hydroxybutyric acid*, $C_{10}H_{13}N_3O_3$ is formed.

This is sparingly soluble in water, easily so in aqueous alkalis and

acids; it melts at 96—98°, and is very unstable. Acetic anhydride is without action on the pseudohydrazide, whilst concentrated sulphuric acid and phosphoric chloride and oxychloride yield resinous products.

Mandelic acid yields with phenylhydrazine a *pseudophenylhydrazidomandelic acid*, $C_{14}H_{14}N_2O_2$, analogous to the butyric compound. It crystallises from alcohol in long, white needles, and melts at 182°.

With lactic acid, only phenylhydrazine lactate was formed.

L. T. T.

Acetylenedicarboxylates and Phenylhydrazine. By E. BUCHNER (*Ber.*, **22**, 2929—2932).—When phenylhydrazine is added to an ethereal solution of methyl acetylenedicarboxylate, *methyl oxalacetate phenylhydrazone*, NHPh·N:C(COOMe)·CH_2·COOMe, is formed. It is easily soluble in boiling alcohol, sparingly soluble in ether, crystallises in colourless, glistening scales, and melts at 118°. Strong sulphuric acid dissolves it to a reddish-yellow solution, which gives a violet-red coloration with ferric chloride or a soluble dichromate. When heated with alkalis or dilute acids, it yields the acid $C_{10}H_8N_2O_3$, obtained by Wislicenus (Abstr., 1887, 235) from the corresponding ethyl-derivative. The latter acid is sparingly soluble in cold water, and forms stable salts. It is probably *phenylpyrazolonecarboxylic acid.* L. T. T.

Weselsky's Resorcinol Dyes. By R. NIETZKI, A. DIETZE, and H. MÄCKLER (*Ber.*, **22**, 3020—3038).—Resazurin (Weselsky's diazoresorcinol), $C_{12}H_7NO_4$, is obtained, together with resorufin (diazoresorufin) by Weselsky and Benedikt's method (*Monatsh.*, **1**. 889), and can be purified by means of the sodium salts. It crystallises from glacial acetic acid in small, greenish prisms, which do not melt without decomposition. The *sodium salt*, $C_{12}H_6NO_4Na$, crystallises in long, green, lustrous needles rather readily soluble in water, sparingly in aqueous sodium carbonate and sodium chloride. In thin layers the solution is almost pure blue and shows, especially in presence of a little alcohol, a splendid, brick-red fluorescence. The *barium salt* forms brownish, sparingly soluble needles; the *silver salt* is a voluminous, flaky precipitate. The *ethyl*-derivative crystallises in long, dark-red needles melting at 215°. The *acetyl*-derivative, $C_{12}H_6NO_4Ac$, prepared by heating a mixture of sodium resazurin and sodium acetate (dry) with acetic anhydride (12—15 parts), crystallises from alcohol in long, ruby-coloured needles melting at 222°; when heated with sodium carbonate, blue resazurin is formed. Tetrabromoresazurin, $C_{12}H_3Br_4NO_4$ (Weselsky and Benedikt's "non-fluorescent blue") was prepared by brominating resazurin; the *sodium salt*, $C_{12}H_2Br_4NO_4Na + 2H_2O$, crystallises from hot, dilute alcohol in lustrous, green needles. When the bromo-derivative is reduced, tetrabromoresorufin is formed, as observed by Weselsky and Benedikt; the potassium salt has the formula they ascribed to it, $C_{12}H_2Br_4NO_4K + 2H_2O$.

The substance obtained by the action of acetic chloride on resazurin, to which Brunner and Krämer ascribed the formula, $C_{12}H_9Cl_2NO_3$

(Abstr., 1884, 1333), crystallises in golden plates, and seems to be a mixture.

Resorufin, $C_{12}H_7NO_3$, was obtained from the mother liquors from the preparation of resazurin, and also by heating the latter with hydrogen sodium sulphite solution. It crystallises in small, brown needles. The *potassium salt* forms small, brownish plates, extremely soluble in water; the *ethyl salt*, $C_{12}H_6NO_3Et$, crystallises in orange-red needles melting at 225°. The acetyl-compound crystallises in long needles, melts at 223°, and has the formula given to it by Weselsky and Benedikt. Tetrabromoresorufin ("fluorescent blue") was prepared in a manner similar to tetrabromoresazurin; the *sodium salt*, $C_{12}H_2Br_4NO_3Na + 2H_2O$, crystallises in splendid, lustrous, green needles.

Hydroresorufin, the compound obtained by the action of zinc chloride on resorufin or on resazurin, has the formula $C_{12}H_9NO_3$. It crystallises in nearly colourless, wide needles, which soon become green when exposed to air. The *triacetyl-compound*, $C_{12}H_6NO_3Ac_3$, forms long, colourless, lustrous needles, melts at 216°, and is nearly insoluble in water, sparingly soluble in hot alcohol, and very soluble in hot glacial acetic acid. The molecular weight of the acetyl-derivative was determined by Raoult's method. When hydroresorufin is distilled with zinc-dust, diphenylamine is formed.

The paper concludes with remarks on the constitution of resorufin and resazurin. N. H. M.

Dyes of the Benzeïn Group. By K. Heumann and H. Rey (*Ber.*, **22**, 3001—3004).—*Tetramethylrosamine*, $C_{23}H_{23}N_2(OH)_3$ (?), is prepared by the action of benzotrichloride (1 mol.) on dimethylmetamidophenol (2 mols.) at 50—60°, using sand or benzene as a diluent to keep down the temperature; the reaction is completed by heating at 60° on a water bath. The product is steam-distilled, extracted with boiling water containing hydrochloric acid, and precipitated with sodium chloride. It is purified by dissolving in water, partially precipitating with sodium carbonate, filtering, and precipitating with sodium carbonate or ammonia. The *hydrochloride*, $C_{19}H_{11}Me_4N_2OCl$, forms black-red needles with steel-blue reflection; the *platinochloride* is a dark red precipitate soluble in water; the *oxalate* and *nitrate* form dark green and steel-blue needles respectively. The aqueous solutions of the salts have a splendid bluish-red colour with yellowish-red fluorescence. The solution in sulphuric acid is orange-yellow, the colour being changed to red by the addition of water. Silk and wool are coloured rose-colour to dark-red by a slightly acid bath of the dye. The colour on silk and jute shows a yellowish-red fluorescence, which is increased by sulphuric acid.

The rosamines are decolorised by zinc-dust in acid and alkaline solutions. Addition of soda does not produce an immediate precipitate in solutions of the dyes; a sodium salt seems to be formed. The alkaline solutions dye unmordanted wool an intense rose-colour, or even deep-red, but the colour is removed by boiling soap solution, or by prolonged boiling with water.

Tetrethylrosamine was also prepared from diethylmetamidophenol

and benzotrichloride. The salts produce a bluer colour than those of the methyl-derivatives.

Diphenylrosamine, from metahydroxydiphenylamine, is a violet dye, readily soluble in alcohol, sparingly in water. N. H. M.

Action of Chlorocarbonylamide (Urea Chloride) on Aromatic Hydrocarbons in the Presence of Aluminium Chloride. By E. P. HARRIS (*Chem. Centr.*, 1889; ii. 285—286).—The following compounds are obtained by gently warming chlorocarbonylamide with the corresponding hydrocarbons and finely-powdered aluminium chloride. *Metaxylamide*, $C_6H_3Me_2{\cdot}CO{\cdot}NH_2$, forming lustrous needles melting at 180°, from which Fittig's xylic acid is obtained by saponifying with alcoholic potash. *Orthoxylamide*, crystallising in lustrous needles and melting at 136—137°, from which Fittig's paraxylic acid is obtained by hydrolysis. *β-Isodurylamide*, $C_6H_2Me_3{\cdot}CO{\cdot}NH_2$, forming lustrous plates melting at 184°. *Tetramethylbenzamide*, $C_6HMe_4{\cdot}CO{\cdot}NH_2$, crystallising in plates melting at 172—173°. *Acenapthenecarboxylamide*, $C_{13}H_{11}ON$, forming plates melting at 198°. *α-Ethylnaphthalenecarboxylamide*, $C_{10}H_6Et{\cdot}CO{\cdot}NH_2$, crystallising in colourless needles melting at 166°. All these amides are readily hydrolysed, the corresponding acids being formed. Alkaline potassium permanganate oxidises acenaphthenecarboxylic acid to naphthalenetricarboxylic acid. In the case of the homologues of benzene, the amidocarbonyl group enters in the para-position, unless this is already occupied, in which case it assumes the meta-position. In the case of the homologues of naphthalene only the α-derivatives react with chlorocarbonylamide. J. W. L.

Behaviour of Aniline towards Substitution-derivatives of Hydroxybenzoic Acids at High Temperatures. By H. LIMPRICHT (*Ber.*, **22**, 2906—2912). The author, before examining the action of aniline on substituted hydroxybenzoic acids, repeated other experimenters' work on the action of aniline (14 grams) on the hydroxybenzoic acids (10 grams). With the ortho-acid, 1·5 grams of anilide were obtained, with the para-acid, 1 gram of anilide, whilst with the meta-acid apparently nearly all the hydroxy-acid was converted into the anilide. Contrary to Kupferberg's statement, the author finds that salicylanilide distils at a high temperature without decomposition.

L. T. T.

Action of Aniline on Amidosalicylic Acid. By H. LIMPRICHT and v. RECHENBERG (*Ber.*, **2**, 2908—2912).—Amidosalicylic acid [OH : COOH : NH_2 = 1 : 2 : 4] is best obtained by heating azobenzenesalicylic acid with stannous chloride. When amidosalicylic acid is heated with aniline hydrochloride at 160—210° for some hours, it yields *phenamidophenol*, $NHPh{\cdot}C_6H_4{\cdot}OH$, and *diphenamidophenylene*, $C_6H_4(NHPh)_2$. The former is soluble in cold alcohol, the latter only in boiling alcohol. Phenamidophenol crystallises from water in large, flat, colourless prisms, which turn brown on exposure to the air. It melts at 70°, and distils almost without decomposition. It is soluble in soda, and is coloured blue by strong nitric acid. With ethyl iodide and alcohol, it yields a derivative which was not, however,

obtained in a pure state. With excess of acetic anhydride, it yields *diacetylphenamidophenol*, $OAc{\cdot}C_6H_4{\cdot}NPhAc$, which forms white crystals soluble in alcohol, ether, and benzene, and melts at 119°. *Phenamidophenolsulphonic acid*, $SO_3H{\cdot}C_6H_3(OH){\cdot}NHPh$, obtained by heating the phenol with strong sulphuric acid, crystallises from boiling water in small, grey prisms, which are still solid at 260°. It is easily soluble in alcohol, sparingly so in ether and benzene. The barium salt is crystalline. Diphenamidophenylene, obtained as above, forms grey or brownish needles, easily soluble in ether, chloroform, acetone, benzene, carbon bisulphide, acetic acid, and boiling alcohol, insoluble in water, and melts at 141°. Nitric acid gives first a blue and then a blood-red coloration, concentrated sulphuric acid dissolves the crystals to a blue solution; hydrochloric acid has no action, but if sodium nitrite is added to the mixture, an unstable *nitroso*-derivative is formed. Diphenamidophenylene is not formed by the action of pure aniline on phenamidophenol, but only when hydrochloric acid or aniline hydrochloride is present. Both the phenol and phenylene are *para*-compounds, and they can also be similarly prepared from the [1 : 3 : 4] amidosalicylic acid. L. T. T.

Aromatic Substituted Pseudothiocarbamides. By B. Prager (*Ber.*, **22**, 2991—3001).—*Phenylpropylene-ψ-thiocarbamide*,

$$NHPh{\cdot}C\Big\langle\begin{matrix}S{\cdot}CHMe\\ |\\ N{\cdot}CH_2\end{matrix},$$

is prepared by heating allylphenylthiocarbamide (m. p. 95°, 50 grams) with crude hydrochloric acid (100 c.c.) for two hours at 100°. The product is evaporated down, diluted with water, and saturated with ammonia. It melts at 117°, and dissolves readily in chloroform, alcohol, ether, and benzene. The *picrate* crystallises in yellow needles melting at 154°; the *platinochloride*, $(C_{10}H_{12}N_2S)_2,H_2PtCl_6$, forms microscopic, yellow crystals.

Phenyl-β-methyltaurocarbamic anhydride, $C_{10}H_{12}N_2SO_3$, is formed when the above base is oxidised with potassium chlorate and hydrochloric acid (Andreasch, Abstr., 1883, 664). It melts at 192°, dissolves in alcohol and glacial acetic acid, sparingly in hot water, and is indifferent to acids and alkalis. When heated with hydrochloric acid at 230° for five hours it is converted into β-methyltaurine (Gabriel, Abstr., 1889, 848) and aniline.

Phenylmethylpropylene-ψ-thiocarbamide, $NMePh{\cdot}C\Big\langle\begin{matrix}S{\cdot}CHMe\\ |\\ N{\cdot}CH_2\end{matrix}$, is obtained when a mixture of methylaniline (30 grams) and allylthiocarbamide (30 grams) is heated for a short time, then left for some hours, and finally heated with hydrochloric acid (120 c.c.) at 100° for two hours (compare Gebhardt, Abstr., 1885, 383). The base was not obtained pure by this method, but salts were prepared. The base was also prepared by the action of an excess of methyl iodide on phenylpropylenethiocarbamide. It distils at about 300° without decomposition. The *picrate* crystallises from boiling water in yellow needles melting at 125°; the *platinochloride* separates from the dilute hydro-

chloric acid solution in orange-red crystals melting at 183—184° with decomposition.

When phenylmethylpropylenethiocarbamide is oxidised with potassium chlorate and hydrochloric acid and the product heated with hydrochloric acid at 150—160°, β-methyltaurine and methylaniline are formed.

Allylorthotolylthiocarbamide, $C_{11}H_{14}N_2S$, is prepared by heating a mixture of orthotoluidine (25 grams) dissolved in alcohol (20 c.c.) and allylthiocarbamide (25 grams) and evaporating the product on a water-bath. It forms lustrous crystals, melts at 98°, dissolves readily in glacial acetic acid, chloroform, alcohol, and benzene, is less soluble in alcohol, and insoluble in water.

Orthotolylpropylene-ψ-thiocarbamide, $C_7H_7{\cdot}NH{<}\begin{matrix}S{\cdot}CHMe\\ |\\ N{\cdot}CH_2\end{matrix}$, obtained from the above compound by the action of hydrochloric acid, crystallises in small, rhombic plates, melts at 126°, dissolves readily in the usual organic solvents, and in mineral acids, sparingly in hot water. The *picrate* melts at 175—176°; the *platinochloride* forms orange-red crystals melting at 177—178°.

Orthotolylmethylpropylene-ψ-thiocarbamide, $C_7H_7{\cdot}NMe{<}\begin{matrix}S{\cdot}CHMe\\ |\\ N{\cdot}CH_2\end{matrix}$, formed by the action of methyl iodide on orthotolylpropylenethiocarbamide, boils at about 295°. The *hydriodide* crystallises in long hexagons melting at 165—166°; the *picrate* forms yellow prisms melting at 137—138°; the *platinochloride* decomposes at above 200°. When the base is oxidised and the product heated with hydrochloric acid, β-methyltaurine is formed.

α-Naphthylpropylene-ψ-thiocarbamide, $C_{14}H_{14}N_2S$, obtained from allyl-α-naphthylthiocarbamide (m. p. 145°, not 130°; Zinin, *Annalen*, **34**, 346), crystallises in rhombic plates, melts at 134°, dissolves readily in chloroform, alcohol, and benzene, is less soluble in ether, and insoluble in light petroleum and water. The *picrate* crystallises in long, rectangular prisms melting at 192°; the *platinochloride* is an orange-coloured, crystalline salt which melts at 205—206° with effervescence.

N. H. M.

Piaselenoles and Piazothioles. By O. HINSBERG (*Ber.*, **22**, 2895—2902).—Continuing his previous work (Abstr., 1889, 785), the author finds that selenious anhydride or acid reacts with aromatic orthodiamines to form piaselenoles, but that no similar derivatives are formed from aromatic meta- or para-diamines or from fatty diamines. Sulphurous anhydride forms a similar series of *piazothioles* with aromatic ortho-diamines, but phosphorous, boric, and tellurous anhydrides, phosphorous chloride, phosphoric oxychloride, and arsenious chloride do not yield any analogous compounds. The piaselenoles and piazothioles closely resemble many of the substituted quinoxalines.

Piaselenole, $C_6H_4{:}N_2{:}Se$, prepared from orthophenylenediamine, forms colourless needles easily soluble in alcohol, ether, and benzene, sparingly so in water; when heated it melts at 76° and emits an odour

resembling that of quinoxaline. Its salts are yellow in colour and are decomposed by excess of water. Sodium yields a characteristic green periodide. *Ethoxypiaselenole*, $OEt\cdot C_6H_3⋮N_2⋮Se$, prepared from ethoxyphenylenediamine, crystallises in pale, yellowish needles, soluble in alcohol, and melting at 103—104°. With concentrated sulphuric acid it yields an intensely yellow solution; with stannous chloride and potassinm periodide it behaves like the other piaselenoles. *Amidopiaselenole*, $NH_2\cdot C_6H_3⋮N_2⋮Se$, unlike the other piaselenoles, is only formed when selenious acid and triamidobenzene (1 : 2 : 4) solutions are mixed in the cold; at higher temperatures, the triamidobenzene acts as a reducing agent towards the selenious acid. It crystallises in brownish-red needles, soluble in alcohol, benzene, and ether, sparingly so in water, and melting at 149—150°. Its salts are dark-brown and crystalline, but are rather unstable. Concentrated sulphuric acid dissolves it, forming an almost colourless solution, with a reddish fluorescence, but it becomes intensely brown on dilution.

Piazothiole, $C_6H_4⋮N_2⋮S$, is formed when orthophenylenediamine is heated with concentrated aqueous sulphurous acid (or sodium hydrogen sulphite) for five or six hours at 180—200°. It is also formed when a stream of sulphurous anhydride is passed into the boiling diamine, but its formation is then generally accompanied by that of resinous bye-products. It forms colourless crystals having a strong odour resembling that of quinoxaline, melts at 44°, boils at 206° (uncorr.), distils in a current of steam, is sparingly soluble in boiling water, easily so in organic solvents, and is only feebly basic in character, its solutions in strong mineral acids being precipitated on the addition of water. Piazothiole is a very stable substance, and very resistent to oxidation; strong reducing agents convert it into phenylenediamine and hydrogen sulphide. *Methylpiazothiole*, $C_6H_3Me⋮N_2⋮S$, from metaparatoluylenediamine resembles piazothiole in character, melts at 34°, and boils at 233—234° (uncorr.). Determination of its molecular weight by Raoult's method gave 143, the formula $C_7H_6N_2S$ requiring 150. Its salts are colourless and are decomposed by water. The *platinochloride*, $(C_7H_6N_2S)_2,H_2PtCl_6$, forms reddish-yellow crystals; the periodide is also crystalline. When methylpiazothiole is dissolved in strong sulphuric acid and strong nitric acid then added in excess, *nitromethylpiazothiole*, $NO_2\cdot C_6H_2Me⋮N_2⋮S$, is obtained. It forms colourless crystals, soluble in alcohol and glacial acetic acid, and melting at 154—156°. *Bromomethylpiazothiole*, $C_6H_2MeBr⋮N_3⋮S$, formed by the addition of bromine to a cold chloroform or hot acetic acid solution of methylpiazothiole, forms white needles melting at 98°. It is volatile in steam and is very stable, the bromine-atom not being removed by boiling with potash.

L. T. T.

Derivatives of Paranitrocinnamaldehyde. By A. EINHORN and C. GEHRENBECK (*Annalen*, **253**, 348—376; compare Abstr., 1889, 396).—*Paranitrocinnamaldoxime*, $NO_2\cdot C_6H_4\cdot C_3H_3⋮N\cdot OH$, prepared by boiling the aldehyde with hydroxylamine hydrochloride and sodium carbonate in dilute alcoholic solution, is a yellow, crystalline compound melting at 178—179°. The *anilide*, $C_{15}H_{12}N_2O_2$, crystallises from alcohol in yellow needles melting at 132—133°.

Paranitro-α-bromocinnamaldehyde (m. p. 136°), identical with the compound obtained by Zincke and Hagen (Abstr., 1884, 1343), by nitrating α-bromocinnamaldehyde, is formed when nitrocinnamaldehyde is treated with bromine in glacial acetic acid solution; the dibromide could not be obtained in a pure condition.

Paranitrophenylbutine methyl ketone,

$$NO_2\cdot C_6H_4\cdot CH\!:\!CH\cdot CH\!:\!CH\cdot COMe,$$

is obtained, together with paradinitrodiphenyldibutine ketone, when paranitrocinnamaldehyde is treated with acetone in alcoholic soda solution; the filtrate from the paradinitro-compound is poured into acidified water, the precipitate digested with dilute sodium carbonate solution to free it from paranitrocinnamic acid and recrystallised. It separates from water in colourless needles, melts at 132°, and is readily soluble in the ordinary solvents. The *hydrazone*, $C_{16}H_{17}N_3O_2$, separates from alcohol in ruby-red crystals melting at 209—210°.

Paradinitrodiphenyldibutine ketone, $CO(CH\!:\!CH\cdot CH\!:\!CH\cdot C_6H_4\cdot NO_2)_2$, crystallises from acetic anhydride in pale yellow needles, melts at 216—218°, and is readily soluble in glacial acetic acid but insoluble in water, ether, chloroform, and alcohol.

Paranitrophenylbutinecarboxylic acid (compare Einhorn and Gehrenbeck, *loc. cit.*) can be prepared by gradually adding an alcoholic solution of paranitrophenylbutine methyl ketone to a boiling, concentrated solution of sodium hypochlorite. The *ethyl* salt, $C_{13}H_{13}NO_4$, crystallises from alcohol in yellowish plates, melting at 118°. The *copper* salt, $C_{22}H_{16}N_2O_8Cu$ is crystalline, the *silver* salt, $C_{11}H_8NO_4Ag$, amorphous; the alkaline salts are very readily soluble in water.

Paranitrophenylbutine-ω-dicarboxylic acid (m. p. 208°) is readily soluble in alcohol, hot water, and glacial acetic acid, but sparingly in benzene, ether, and chloroform. The *ethyl* salt, $C_{16}H_{17}NO_6$, crystallises from dilute alcohol in colourless needles melting at 104—105°. The *copper* salt, $C_{12}H_7NO_6Cu$, is crystalline, the *silver* salt. $C_{12}H_7NO_6Ag_2$, amorphous, and the alkaline salts are very readily soluble in water.

Paranitrophenyl-$\gamma\delta$-dibromethyl-β-bromacrylic acid is readily soluble in ether, ethyl acetate, and alcohol, but only sparingly in chloroform and benzene; when oxidised with 3 per cent. potassium permanganate, it yields paranitrobenzoic acid. The *ethyl* salt $C_{13}H_{12}NBr_3O_4$, crystallises from alcohol in colourless plates melting at 124°. The *sodium* salt crystallises with 2 mols. H_2O. F. S. K.

Constitution of Filicic Acid. By H. SCHIFF (*Annalen*, **253**, 336—342).—The author discusses the results obtained by Grabowski (*Annalen*, **143**, 279), Luck (Abstr., 1889, 276), and Daccomo (*ibid.*, 54) in their investigations of filicic acid, and comes to the conclusion that filicic acid is a butyrophloroglucyl allyl ketone of the constitution $\begin{matrix} C(OH)\!:\!CH\cdot C\cdot O\cdot CH_2\cdot CHMe_2 \\ | \qquad\qquad\quad \| \\ CH\!:\!C(OH)\cdot C\cdot CO\cdot CH_2\cdot CH\!:\!CH_2 \end{matrix}$. The criticisms of Paterno (Abstr., 1889, 615) on the experimental results of Daccomo (*loc. cit.*)

would seem, according to the author, to be to a great extent ungrounded. F. S. K.

Carbothionylic Acids of Resorcinol and Pyrogallol. By E. LIPPMANN (*Monatsh.*, **10**, 617—623; compare Abstr., 1888, 1092).—*Dihydroxydithiobenzoic acid*, $C_6H_3(OH)_2\cdot CSSH$, is obtained in 60 per cent. of the theoretical yield by heating in a closed flask for 12 hours at 100° a mixture of resorcinol (50 grams) and potassium xanthate (80 grams). On heating the acid (50 grams) at 130—140° with potash (250 grams) dissolved in a little water, it is converted into β-resorcylic acid and consequently must be regarded as a metacarbothionylic acid.

Pyrogallolcarbothionylic acid, $C_6H_2(OH)_3\cdot CSSH + H_2O$, is prepared in a manner precisely similar to that used in the case of dihydroxydithiobenzoic acid. It crystallises unchanged from dilute alcohol in the form of beautiful, glistening, golden scales, which become anhydrous at 70° and melt at 154°. On heating it with five times its weight of potash and a little water at 120—130°, it gives the pyrogallolcarboxylic acid of Senhofer and Brunner, and consequently has the constitution $CSSH : (OH)_3 = 1 : 2 : 3 : 4$. G. T. M.

Action of Orthonitrocinnamaldehyde on Malonic Acid. By A. EINHORN and C. GEHRENBECK (*Annalen*, **253**, 374—376).—*Orthonitrophenylbutine-ω-dicarboxylic acid*, $C_{12}H_9NO_6$, prepared by heating orthonitrocinnamaldehyde with malonic acid for six hours in glacial acetic acid solution, crystallises from glacial acetic acid in yellowish needles, melts at 212—213°, and is sparingly soluble in benzene, ether, and chloroform, but readily in alcohol and hot water. The *silver* salt, $C_{12}H_7NO_6Ag_2$, crystallises in yellowish plates; the copper salt, $C_{12}H_7NO_6Cu$, is a yellowish-green, crystalline compound.

Orthonitrophenylbutene-α-hydroxy-ω-dicarboxylic acid,

$$NO_2\cdot C_6H_4\cdot CH\colon CH\cdot CH(OH)\cdot CH(COOH)_2,$$

is the first product of the action of malonic acid on orthonitrocinnamaldehyde; it crystallises from alcohol, in which it is only sparingly soluble, in colourless needles, melts at 269°, explodes when heated strongly, and is insoluble in benzene and light petroleum, and only sparingly soluble in ether, chloroform, and glacial acetic acid, but readily in hot water. F. S. K.

Benzoyltannin. By C. BÖTTINGER (*Ber.*, **22**, 2706—2709).—*Benzoyltannin* can be obtained by shaking an aqueous solution of tannin with soda and benzoic chloride; the dirty-white precipitate which is produced is boiled with ether to free it from benzoic acid, and the residue is warmed to expel the ether, washed with water, and dried. It is a pale yellow, crystalline powder, insoluble in boiling water, and almost insoluble in boiling alcohol. It is not acted on by ammonia, and it is only very slowly dissolved and decomposed by cold dilute soda. When heated with water at 150°, it liquefies com-

pletely, but it is only partially decomposed even after heating for two hours at 165°. It dissolves in hot aniline with formation of benzanilide, and is soluble in hot dimethylaniline. It is decomposed by warm, concentrated sulphuric acid or when heated alone. It dissolves in warm phenylhydrazine with slight evolution of gas, yielding a yellow substance and a crystalline compound which is soluble in ether and in boiling soda.

Other naturally occurring tannic acids give similar benzoyl-derivatives.

Tannin dissolves in warm, concentrated sulphuric acid, and is thereby converted into gallic acid.

The benzoyl-derivative of tannic acid (from oak bark) dissolves in warm phenylhydrazine with evolution of gas, yielding a yellowish-brown substance which is soluble in soda. F. S. K.

Tannins. By C. Etti (*Monatsh.*, **10**, 647—664).—Investigation of the tannins of the formulæ $C_{17}H_{16}O_9$ and $C_{20}H_{20}O_9$ (compare Abstr., 1881, 277; 1883, 994) has proved that they are not glucosides, but are to be regarded as derivatives of a ketonic acid,

$$C_6H_2(OH)_3{\cdot}CO{\cdot}C_6H(OH)_3{\cdot}COOH.$$

The author has now isolated a new tannin, which resembles those above mentioned in its general chemical and physical properties, appearing from its behaviour with phenylhydrazine and hydroxylamine to be also a ketonic compound. It has the formula $C_{16}H_{14}O_9$, and is obtained as a red powder from the diluted extract of the wood of the common Slavonian oak by careful precipitation with hydrochloric acid (excess of acid must be avoided, as it diminishes the yield). The precipitate is allowed to remain for several days, then collected, well washed with water, air dried, and, lastly, fractionally dissolved by alcoholic solutions of different strengths and precipitated with water. The pure substance, which is brownish-red, is made up of microscopic, warty, spherical masses (recrystallised from alcohol), insoluble in water and ether, but readily soluble in acetone, and has been shown by Fuchs (*Monatsh.*, **9**, 1132—1142) to be a monobasic acid. With phenylhydrazine, it gives a yellow, amorphous compound, $C_{22}H_{20}N_2O_8$, forms a brown amorphous oxime, $C_{16}H_{15}NO_9$, and when heated with dilute sulphuric acid (1 : 10) for six hours in a sealed tube at 120—130°, yields, together with an insoluble anhydride, a red solution, from which, by extraction with ether, a red, crystalline mass may be obtained. On pressing this and recrystallising from water, it becomes colourless, and is identical with gallic acid (m. p. 238—240°). On treatment with magnesia, the tannin, $C_{16}H_{14}O_9$, gives the following salts:—$(C_{16}H_{13}O_9)_2Mg$, a brownish-yellow, amorphous mass; $(C_{16}H_{10}O_9)_2Mg_4$ and $(C_{14}H_{11}O_9)_2Mg_3$, both bright-yellow powders scarcely soluble in water; $(C_{16}H_{13}O_9)_2Mg + 2C_{16}H_{14}O_9$, of a brownish-yellow colour and very soluble in water. In all probability, the extract furnishing the tannin contains it as a soluble normal magnesium salt.

The tannin, $C_{16}H_{14}O_9$, when heated alone at 130—135°, or in closed

tubes with water at 100°, loses water, forming anhydrides, from which the acid cannot be again regenerated, and which yield methyl iodide on boiling with hydriodic acid. On boiling the tannin with dilute sulphuric acid in an open vessel, an acid of the formula $C_{32}H_{24}O_{16} = 2C_{16}H_{14}O_9 - 2H_2O$ is formed as a reddish, insoluble mass, whilst, on heating in a closed tube, two anhydrides are formed, of which one, $C_{32}H_{20}O_{14}$, of a dark-red colour, is soluble in 95 per cent. alcohol, and, according to Fuchs (*loc. cit.*), is of an acid nature, whilst the other, $C_{32}H_{18}O_{13}$, which is blackish, is insoluble, and shows no acid reaction. The tannin, $C_{16}H_{14}O_9$, on long heating with hydrochloric acid at 100°, loses a methoxyl-group, and is converted into an acid, $C_{15}H_{12}O_9$, of a yellow colour, which still contains a methoxyl-group; so that the tannin itself contains two methoxyl-groups.

G. T. M.

Dibromosulphanilic Acid and its Derivatives. By O. HEINICHEN (*Annalen*, **253**, 267—288).—Dibromosulphanilic acid can be conveniently prepared by gradually adding a freshly prepared solution of bromine (10 c.c.) and soda (16 grams) in water (150 c.c.) to a hot, aqueous (500 c.c.) solution of sulphanilic acid (17·3 grams) and 35 per cent. hydrochloric acid (21 grams); the yield of the barium salt is 39·9 grams, or 95 per cent. of the theoretical. It can also be prepared by gradually adding a solution of potassium bromate (11·1 grams) in water (250 c.c.) to a hot, aqueous solution (500 c.c.) of sulphanilic acid (17·3 grams) and 43 per cent. hydrobromic acid (37·6 grams); the yield of the barium salt is 38 grams, or 90 per cent. of the theoretical, and no tribromaniline is formed in the reaction.

Sulphanilic acid is converted into aniline, but only very slowly, when it is heated at 200—220° with dilute sulphuric acid (b. p. 160°) in a current of steam. Dibromosulphanilic acid, at a temperature of about 170—178°, other conditions remaining the same, is readily converted into dibromaniline (m. p. 83—84°); the yield is 83 per cent. of the theoretical.

Dibromaniline [$Br_2 : NH_2 = 1 : 3 : 2$] crystallises from hot, dilute alcohol in long, colourless needles, melts at 83—84°, sublimes at 262—264°, and is readily soluble in alcohol, ether, benzene, and chloroform. The *hydrochloride*, prepared by passing hydrogen chloride into a benzene solution of the base, melts at 126°, and is decomposed by alcohol and by water, or by exposure to the air. The *platinochloride*, $(C_6H_3Br_2{\cdot}NH_2)_2,H_2PtCl_6$, crystallises in golden plates and is decomposed by water.

Diazodibromobenzene sulphate, $C_6H_3Br_2N_2,HSO_4$, prepared by treating dibromaniline with sulphuric acid and ethyl nitrite in well-cooled alcoholic solution, crystallises in colourless needles, and is, relatively, very stable; when boiled with water under reduced pressure, it yields an oil, probably metadibromobenzene, but when heated with sulphuric acid (b. p. 150°), it is converted into dibromophenol (m. p. 55—56°).

Metadibromoquinone [$O_2 : Br_2 = 1 : 4 : 2 : 6$] is obtained when dibromosulphanilic acid is oxidised with potassium chromate and

sulphuric acid in the cold. It crystallises from hot alcohol in golden, iridescent plates, melts at 131°, and is readily soluble in alcohol, ether, chloroform, and benzene, but only very sparingly in cold water. The same compound is obtained by oxidising dibromoparamidophenol; this quinone is probably identical with the dibromoquinone obtained by Levy and Schultz (Abstr., 1882, 509) by oxidising tribromophenol with fuming nitric acid. F. S. K.

Tin Tetraphenyl. By A. Polis (*Ber.*, **22**, 2915—2918).—500 grams of a tin-sodium alloy (25 per cent. of sodium and 75 per cent. of tin), 600 grams of bromobenzene, and 25 c.c. of ethyl acetate were heated together at incipient boiling for about 30 hours. The product was a syrupy, brown mass, the solution of which in boiling benzene deposited crystals of *tin tetraphenyl*, $SnPh_4$, on cooling. This substance when pure forms thin, colourless prisms belonging to the tetragonal system, $a : c = 1 : 0·3893$; $111 : 110 = 70° 35'$. It is thus isomorphous with silicon tetraphenyl and lead tetraphenyl, the axial ratios following the order corresponding with the positions of the metals in the periodic system. It melts at 225—226°, volatilises unchanged, and boils above 420°.

It resembles the corresponding silicon and lead compounds in solubility, dissolving readily in boiling benzene, glacial acetic acid, chloroform, and carbon bisulphide; very sparingly in alcohol and ether. It inflames spontaneously when exposed to air. When treated with bromine (2 mols.), bromobenzene and tin diphenyl dibromide are formed. The author finds that under 42 mm. pressure the latter compound distils at 230° without decomposition. Chlorine is similar in its action to bromine, whilst iodine is without action.

L. T. T.

Derivatives of Diphenyline. By J. Reuland (*Ber.*, **22**, 3011—3019).—*Dibenzylidenediphenyline*, $C_{12}H_8(N\dot{:}CHPh)_2$, is prepared by heating a mixture of diphenyline (1 mol.) and benzaldehyde (2 mols.) on a water-bath for several hours until clear, dissolving the product in ether and precipitating with light petroleum. It crystallises from alcohol and benzene in lustrous, yellow plates, melts at 232—233°, and is sparingly soluble in alcohol and ether. It was not analysed.

Dimetanitrobenzylidenediphenyline, $C_{12}H_8(N\dot{:}CH·C_6H_4·NO_2)_2$, prepared by heating diphenyline (1 mol.) dissolved in a little alcohol with metanitrobenzaldehyde (2 mols.) for some time on a water-bath, crystallises from a mixture of benzene and alcohol as a fine, yellow, crystalline powder. It melts at 184—185°, and is readily soluble in benzene, less so in alcohol. The *diparanitro-derivative*, $C_{26}H_{18}N_4O_4$, is a yellowish-red powder, melting at 208°.

Diorthohydroxybenzylidinediphenyline, $C_{12}H_8(N\dot{:}CH·C_6H_4·OH)_2$ prepared from diphenyline and salicylaldehyde, crystallises from alcohol in yellow plates, melting at 145°.

Difurfuraldiphenyline, $C_{12}H_8(N\dot{:}C_5H_4O)_2$, is formed when furfuraldehyde (3 grams) is added to a solution of diphenyline (3 grams) in absolute alcohol (100 grams) and kept for 24 hours. It crystallises in

lustrous, yellow plates, and melts at 137°. When the alcoholic solution is treated with mineral acids, splendid, red compounds are formed.

Phthalodiphenyline, $C_{12}H_8(N{:}C<^{C_6H_4}_{O\,-}>CO)_2$, obtained by heating diphenyline with phthalic anhydride (2 mols.) for two hours at 115—120°, crystallises from glacial acetic acid in lustrous, white plates, melting at 255—257°.

Thiocarbodiphenyline, $CS<^{NH\cdot C_6H_4}_{NH\cdot C_6H_4}$, is prepared by heating diphenyline (5 grams) with absolute alcohol (15 grams) and carbon bisulphide (15 grams) for 18—20 hours in a reflux apparatus on a water-bath, distilling off the alcohol and carbon bisulphide, and extracting the residue several times with hot alcohol and ether. It melts at 238° and does not give an odour of thiocarbimide when heated with strong hydrochloric acid.

Diphenylenebisazo-β-naphthol, $C_{12}H_8(N{:}N\cdot C_{10}H_6\cdot OH)_2$, is obtained when diphenyline is dissolved in hydrochloric acid (4 mols.), well cooled, and treated with the calculated amount of sodium nitrite. The tetrazo-compound is filtered and added to a filtered solution of β-naphthol in just sufficient potash. It is crystallised from benzene. It melts at 243—245° and dissolves in strong sulphuric acid with red colour.

Diphenylenebisazoresorcinol, $C_{12}H_8(N{:}N\cdot C_6H_5O_2)_2$, prepared in a manner similar to the above compound, is a reddish-brown powder.

Diphenylenebisazodimethylaniline, $C_{12}H_8(N{:}N\cdot C_6H_4\cdot NMe_2)_2$, is formed as a red precipitate of a metallic lustre by the action of the tetrazo-compound of diphenyline on methylaniline.

Tetramethyldiphenyline, $NMe_2\cdot C_6H_4\cdot C_6H_4\cdot NMe_2$, is obtained by heating dry diphenyline hydrochloride (1 mol.) with methyl alcohol (4 mols.) at 180° for two hours. The product is poured into hydrochloric acid, treated with potash, and extracted with ether; the ether is distilled off, the residue boiled with acetic anhydride and fractionally distilled. The oil, which distils over at 333—345°, solidifies in a short time. It crystallises from absolute alcohol in monoclinic prisms, which are phosphorescent when rubbed together; it melts at 51—52°. It gives a blue coloration with chloranil. The *picrate* crystallises from alcohol in long, red needles, resembling chromic acid, melts at 199—200°, and decomposes at 204°. The *methiodide* forms slightly rose-coloured needles, melts at 184°, and is readily soluble in alcohol and water, almost insoluble in ether. The *dimethiodide* melts at 196° and is readily soluble in water and alcohol.

Diphenylorthoparadicyanide, $C_{12}H_8(CN)_2$ [= 2 : 4′], is prepared by Sandmeyer's method for displacing amido-groups by cyanogen, following exactly the instructions given for benzonitrile (Abstr., 1885, 149). It crystallises in slightly yellowish plates, and melts at 152—153°.

Diphenylorthoparadicarboxylic acid, $C_{12}H_8(COOH)_2$ [= 2 : 4′], obtained by the hydrolysis of the above dicyanide crystallises in colourless plates melting at 251—225°. The *silver salt* is a white powder, melting at 235—237°, readily soluble in ammonia; the *copper salt* is a sparingly soluble, bluish-green, crystalline powder N. H. M.

Oxidation of Triphenylmethane. By M. HANRIOT and O. SAINT-PIERRE (*Bull. Soc. Chim.* [3], **1**, 773—774).—Triphenylmethane, suspected by the authors to contain a higher homologue derived from toluene, was oxidised with chromic mixture; in addition to triphenylcarbinol (20 per cent.) and benzophenone (40 per cent.), small quantities of orthobenzoylbenzoic acid, and of anthraquinone resulting from the dehydration of this acid, were obtained. Pure triphenylmethane yielded neither of the latter substances on oxidation. T. G. N.

Paramethylbenzil and Benzilparacarboxylic Acid. By E. BUCHER (*Ber.*, **22**, 2819—2820).—Paramethyldeoxybenzoïn yields the following bromo-substitution-products:—
$CHPhBr·CO·C_6H_4Me$, $CBr_2Ph·CO·C_6H_4Me$, $CBr_2Ph·CO·C_6H_4·CHBr_2$, and $CBr_2Ph·CO·C_6H_4·CBr_3$, from which *paramethylbenzil*, *dibromodeoxybenzoïnparacarboxylic acid*, $CBr_2Ph·CO·C_6H_4·COOH$, and *benzilparacarboxylic acid* can be obtained.

Paramethylbenzil, $COPh·CO·C_6H_4Me$, is formed when dibromodeoxybenzoïn is heated with water at 180°; it is a yellowish oil.

Benzilparacarboxylic acid, $COPh·CO·C_6H_4·COOH$, is obtained by heating the pentabromide with water at 160°; it crystallises in colourless plates and decomposes at 280—300° without melting.

The acid, $CBr_2Ph·CO·C_6H_4·COOH$, is formed when methyldeoxybenzoïn is heated with bromine (5 mols.) at 160°, or when dibromoparamethyldeoxybenzoïn is heated with bromine (3 mols.) and water at 160°; it crystallises in yellow needles, melts at 218° and is partially converted into benzilcarboxylic acid when heated with magnesia at 190°. F. S. K.

1.4′-Iodonaphthalenesulphonic Acid. By R. MAUZELIUS (*Ber.*, **22**, 2820—2823).—1.4′-*Iodonaphthalenesulphonic* acid, $C_{10}H_6I·SO_3H$, can be prepared by treating α-diazonaphthalenesulphonic acid with warm 40 per cent. hydriodic acid; it is purified by converting it into the chloride (see below) and decomposing the latter with water at 150°. It crystallises in almost colourless plates with 2 mols. H_2O, melts at 129°, and is readily soluble in water. The *potassium* salt,

$$C_{10}H_6I·SO_3K + H_2O,$$

ammonium salt, *sodium* salt, with 1 mol. H_2O, *silver* salt, *copper* salt, with $2H_2O$, and a number of other salts were prepared; they are mostly crystalline and sparingly soluble in water. The *methyl*-salt, $C_{10}H_6I·SO_3Me$, crystallises from alcohol in prisms, melts at 59—60°, and is readily soluble in chloroform and ether, but only sparingly in cold alcohol. The *ethyl*-salt crystallises from alcohol in hexagonal plates, melts at 74° and is readily soluble in chloroform, ether, and benzene. The normal *propyl* salt crystallises in plates and melts at 67°, the *isopropyl* salt in long prisms melting at 90°. The *chloride*, $C_{10}H_6I·SO_2Cl$, crystallises from chloroform in large, monoclinic prisms, melts at 114°, and is readily soluble in hot glacial acetic acid, chloroform, and benzene, but only sparingly in light petroleum. The *bromide* crystallises from benzene and chloroform in short prisms

melting at 153°. The *amide*, $C_{10}H_6I\cdot SO_2\cdot NH_2$, crystallises from alcohol in small scales melting at 239°. F. S. K.

Specific Volumes of Camphor and Borneol. By M. KUHARA (*Chem. News*, **60**, 114).—The camphor employed melted at 177·7° (corr.) and boiled at 205·3° (corr.), the borneol boiled at 209·7° (corr.). Numerous determinations of the specific gravities of these two substances were made, by filling small glass cylinders with them at their respective boiling points and weighing when cold. The sp. gr. of the camphor was found to be 0·8110 at 205·3°, and its sp. vol. 187·42; whilst the mean sp. gr. of the borneol is 0·8083 at 209·7°, and its sp. vol. 190·5. D. A. L.

An Isomeride of Camphor. By O. WALLACH and A. OTTO (*Annalen*, **253**, 249—267; compare this Jour., 1889, 1069, 1071, and 1072).—In preparing pinene nitrosochloride by the method already described (Abstr., 1888, 1098), oily bye-products are formed in considerable quantity, and can be isolated by distilling them with steam in small quantities at a time. The same oily compounds are obtained when ethyl nitrite is used in the place of amyl nitrite; experiments showed that under certain conditions the former can be advantageously employed instead of amyl nitrite in the preparation of nitrosochlorides.

The crude bye-product distils completely between 160 and 190°, the principal portion boiling at 182—188°; it is most probably a mixture of cymene and a compound of the composition $C_{10}H_{16}O$, which the author names *pinole*, as will be shown below.

Pinole dibromide, $C_{10}H_{16}OBr_2$, is obtained in crystals when the fraction boiling at 182—188° is treated with bromine in glacial acetic solution until a permanent coloration is produced and the solution then allowed to evaporate slowly. The mother-liquors from the dibromide contain cymene, which can be isolated by distillation with steam. The dibromide separates from ethyl acetate or alcoholic ether in rhombic crystals, $a:b:c = 0·57:1:1·5553$, melts at 94°, boils at 143—144° (11 mm.), and is moderately easily volatile with steam. It is insoluble in water, but readily soluble in alcohol, ether, chloroform, and ethyl acetate. When boiled with alcoholic potash, it is decomposed, yielding an oil which is readily volatile with steam and very easily soluble in dilute alcohol. This oil can be separated into two principal fractions boiling at 183–184° and at about 210° respectively.

The fraction boiling at 183—184° consists of almost pure *pinole*, $C_{10}H_{16}O$. It has an odour hardly distinguishable from that of cineole, a sp. gr. of 0·953 at 20°, and a refractive power $[\alpha]_D = 1·46949$ at 20°. It combines energetically with bromine, yielding a dibromide (m. p. 94°), also with halogen acids and with nitrosyl chloride, but it does not react with acid chlorides, hydroxylamine, phenylhydrazine, or hydrogen sulphide. It is readily oxidised by warm dilute potassium permanganate solution, yielding carbonic anhydride, oxalic acid, and terebic acid (m. p. 175—176°); nitric acid (1:1) converts it into terebic acid and resinous products. The dibromide gives the

same oxidation-products as pinole itself but it is only very slowly acted on by both the reagents. The constitutional formula,

$$CH\left\langle\begin{array}{c}CHPr^{\beta}\cdot CH_2 \\ \text{———}O\text{———} \\ CH = CMe\end{array}\right\rangle CH,$$

is in accordance with the observed properties of pinole.

The fraction boiling at about 210° consists of impure *pinoleglycol ethyl ether*, $C_{10}H_{16}O(OEt)_2$. This compound can be obtained in colourless, compact needles by fractionating under reduced pressure, cooling the portion boiling at 110—120° (14 mm.) in a freezing mixture, and spreading the crystals on well-cooled porous plates; it is then dissolved in a little glacial acetic acid, the solution poured into water, and the precipitated oil brought into contact with a crystal of the substance.

Pinole nitrosochloride, $C_{10}H_{16}O,NOCl$, is a, relatively, very stable compound melting at 103°; it is readily converted into nitrolamines which generally crystallise well, and thus serve as a means of distinguishing this compound from other nitrosochlorides.

Pinolenitrolamine hydrochloride, $NOH\colon C_{10}H_{15}O\cdot NH_2,HCl$, separates after some time in crystals when the nitrosochloride is treated with excess of alcoholic ammonia; it crystallises well from water and dilute alcohol. The alcoholic mother-liquors from the hydrochloride contain the free *base*, which can be isolated by evaporating under reduced pressure, extracting the residue with chloroform, and distilling the extract under reduced pressure; it is a yellowish liquid, boiling at about 129—130° (14 mm.) with slight decomposition.

Pinolenitrolpiperidine, $NOH\colon C_{10}H_{15}O\cdot C_5NH_{10}$, separates from alcohol in crystals, melts at 154°, and is insoluble in water. The *hydrochloride*, $C_{15}H_{26}O_2N_2,HCl$, is a colourless, crystalline powder very readily soluble in water.

Pinolenitrolbenzylamine, $NOH\colon C_{10}H_{15}O\cdot NH\cdot C_7H_7$, is best obtained in a pure state by decomposing the hydrochloride, as it seems to crystallise from alcohol with 1 mol. of alcohol. It crystallises from ether in transparent prisms, melts at 135—136°, and soon becomes opaque on keeping, but without change in melting point or composition. The *hydrochloride*, $C_{17}H_{24}O_2N_2,HCl$, is crystalline and readily soluble in water.

Pinolenitrolaniline, $NOH\colon C_{10}H_{15}O\cdot NHPh$, crystallises in yellowish plates, melts at 174—175°, and is readily soluble in alcohol and ether. The *hydrochloride*, $C_{16}H_{22}N_2O_2,HCl$, is crystalline and decomposes on exposure to the air.

Pinolenitrol-β-naphthylamine, $NOH\colon C_{10}H_{15}O\cdot NH\cdot C_{10}H_7$, crystallises from alcoholic ether, melts at 194—195°, and is insoluble in water and only sparingly soluble in alcohol; solutions of the base and its salts are highly fluorescent. This compound is isomeric with camphor.
F. S. K.

Preparation of Aloin. By T. WOODRUFF (*Pharm. J. Trans.* [3], **19**, 773—775).—The aloes are exhausted with amyl alcohol at the temperature of a water-bath, when most of the resinous matters

remain in the residue. The liquid is filtered and evaporated and the aloin is obtained as a crystalline mass, contaminated, however, with a small deposit of resinous matters. This product is then exhausted with cold water, the solution is filtered, and the filtrate allowed to evaporate spontaneously, when the crystals are obtained quite pure. R. R.

Cephalanthin, a Bitter. By E. CLAASEN (*Chem. Centr.*, 1889; ii, 258, from *Pharm. Zeit.*, **34**, 384).—The bark of *Cephalanthus occidentalis* (" button bush " or "swamp dogwood"), a bush belonging to the Cinchoneæ, contains a saponin-like substance having a bitter taste and tanning properties. For its separation, the bark is digested with lime, the filtrate treated with carbonic anhydride, and the cephalanthin precipitated from the solution by hydrochloric acid and purified by treatment with alcohol and ether. It is amorphous, sparingly soluble in cold and hot water, readily soluble in alcohol and ether, and has the properties of an acid. When warmed with nitric acid, it gives a yellow coloration, and with concentrated sulphuric acid an orange coloration changing to reddish-brown. Dilute sulphuric acid seems to split up cephalanthin with formation of sugar.
J. W. L.

Digitalin and Tanghinin. By ARNAUD (*Compt. rend.*, **109**, 701—703).—If digitalin is heated in sealed tubes at 180° with water and barium hydroxide, it yields a crystalline compound, which is insoluble in hot water, but somewhat soluble in boiling alcohol. It melts at 305—310° with rapid decomposition. It has the composition $(C_{31}H_{51}O_{11})_2Ba$, and is the barium-derivative of a compound $C_{31}H_{52}O_{11}$, formed from digitalin by the assimilation of water. It follows that the molecule of digitalin is represented by the formula $C_{31}H_{50}O_{10}$.

Tanghinin under similar conditions yields a barium-derivative of the compound $C_{27}H_{44}O_{10}$, which is formed by the assimilation of 2 mols. H_2O by the tanghinin. The molecule of tanghinin is, therefore, represented by the formula $C_{27}H_{40}O_8$. (Comp. Abstr., 1889, 900, and this vol., p. 65.) C. H. B.

Colouring Matters of Chlorophyll. By A. HANSEN (*Ann. Agronom.*, **15**, 428—429; from *Bot. Centr.*, **38**, 632).—The author prepares the yellow and the green constituents of chlorophyll in what he believes to be a pure condition by the following process:—Some leaves of grass are boiled in water for 15—30 minutes, then washed many times with water and dried in the dark. The dry matter is extracted with boiling alcohol, and the solution saponified by boiling three hours with a slight excess of aqueous soda; a current of carbonic anhydride is then passed through the solution, which is afterwards evaporated to dryness on the water-bath. Ether extracts from this soap the yellow colouring matter only, which is purified by evaporating down and crystallising from a mixture of equal parts of ether and light petroleum. The soap, after extraction with ether, is extracted with a mixture of alcohol and ether, which dissolves only traces of the combination of the green colouring matter with soda. On adding

another quantity of alcohol-ether and also phosphoric acid, the green matter is liberated and passes at once into solution, from which it is obtained by evaporation in the form of a brilliant, fragile, greenish-black solid, insoluble in water, benzene, and carbon bisulphide, sparingly soluble in pure ether, very soluble in alcohol with strong red fluorescence. The crystals of yellow colouring matter form orange-red plates insoluble in water, soluble in alcohol, ether, chloroform, and benzene to a deep-yellow colour, and in carbon bisulphide to a brick-red. These crystals are transformed in the light into cholesterin. The author considers this yellow substance to be identical with the yellow colouring matter of flowers and fruits in general, including that of the carrot. J. M. H. M.

Dibromoquinolines. By A. CLAUS and C. GEISLER (*J. pr. Chem.* [2], **40**, 375—382).—1 : 4-Dibromoquinoline has been obtained by Metzger (Abstr., 1884, 757), who asserts that it is identical with La Coste's dibromoquinoline (Abstr., 1881, 74; 1882, 980). When oxidised by potassium permanganate, it yields only pyridinedicarboxylic acid, which is converted into nicotinic acid (m. p. 229°) at 180°. It yields no methiodide, and only one nitro-compound.

Nitro-1 : 4-*dibromoquinoline*, obtained by nitrating the above compound with a cold mixture of two parts of nitric acid (sp. gr. 1·52) and four parts of water, forms colourless, silky needles melting at 155° (uncorr.), and sparingly soluble in water and cold alcohol, but freely in other solvents. The *hydrochloride* forms small, yellowish crystals melting at 228° (uncorr.) when sharply heated. The *platinochloride* is described.

Amido-1 : 4-*dibromoquinoline*, $C_9NH_4Br_2{\cdot}NH_2$, formed by reducing the nitro-compound with stannous chloride and hydrochloric acid in alcohol, distils with steam as small, colourless needles melting at 165° (uncorr.). Bromine converts it into a tribromoquinoline melting at 174° (uncorr.), perhaps identical with Lubavin's (m. p. 173—175°). By directly brominating 1 : 4-dibromoquinoline a tribromide of melting point 115° (uncorr.) and another substance are obtained.

1 : 3-Dibromoquinoline (La Coste, Abstr., 1882, 978) forms no methiodide and only one nitro-compound.

4-*Nitro*-1 : 3-*dibromoquinoline* crystallises in lustrous leaflets which have a greenish shimmer and melt at 162° (uncorr.); it forms well-crystallised, unstable salts. The *platinochloride* is described.

4-*Amido*-1 : 3-*dibromoquinoline* crystallises in needles melting at 184° (uncorr.).

2 : 4-*Dibromoquinoline*, obtained from symmetrical dibromaniline, crystallises in beautiful white, lustrous needles melting at 110° (uncorr.), and freely soluble in the usual solvents except water. The *hydrochloride* forms small, colourless needles melting at 158°. The *platinochloride* is described.

When 2 : 3-dibromaniline is quinolised, two dibromoquinolines are produced, and are separated by crystallising from ether and sorting the crystals.

2 : 3-*Dibromoquinoline* forms prisms which melt at 95° uncorr.; its *hydrochloride* melts at 144° (uncorr.).

3 : 4-*Dibromoquinoline* crystallises in slender needles melting at 124° (uncorr.); its *hydrochloride* and *platinochloride* are described.

A. G. B.

1 : 2-Dibromoquinoline, and Derivatives of 2-Bromoquinoline and 4-Bromoquinoline. By A. CLAUS and G. N. VIS (*J. pr. Chem.* [2], **40**, 382—387).—1-*Nitro-2-bromoquinoline* and 1-*amido-2-bromoquinoline* have been already described as α-nitrometabromoquinoline and α-amidometabromoquinoline, respectively (Abstr., 1889, 281). The 1 : 2 :-amidobromoquinoline *platinochloride* is here described.

1 : 2-*Dibromoquinoline*, obtained by diazotising 1-amidobromoquinoline and treating the diazo-compound with cuprons bromide, crystallises in beautiful, white needles melting at 112° (uncorr.).

4-Bromoquinoline melts at 52°, not 48° (*loc. cit.*); it is best obtained as follows:—The mixture of bromoquinolines prepared from metabromaniline (70 grams) is dissolved in warm dilute nitric acid (1 litre), when 2-bromoquinoline nitrate separates; the mother-liquor is mixed with potash, the precipitated oil dissolved in alcohol (100 c.c.), and a solution of oxalic acid (15 grams) in alcohol (25 c.c.) added; 4-bromoquinoline *oxalate* (m. p. 143°, uncorr.) crystallises out, and is saponified with ammonia to obtain the pure base.

The nitro-4-bromoquinoline melting at 146° (Abstr., 1889, 281) is 3 : 4-*nitrobromoquinoline;* its basic properties are very feeble, so that it is only soluble in concentrated acids, and forms no methiodide. 3 : 4-*Amidobromoquinoline* forms small, yellowish crystals melting at 105° (uncorr.), sparingly soluble in water, and dissolving in dilute acids with an intensely red colour; it gives the carbylamine reaction with alcoholic potash. Its *platinochloride* is described. A. G. B.

Bromine-derivatives of Quinoline. By A. CLAUS and A. WELTER (*J. pr. Chem.* [2], **40**, 387—395).—The authors point out that La Coste's bromoquinoline (Abstr., 1881, 741) is not 3-bromoquinoline but 4′-bromoquinoline, and that the dibromoquinoline obtained from it is not identical with 1 : 4-dibromoquinoline, already described (above abstract); the former dibromoquinoline can also be obtained by brominating 4′-bromoquinoline, and is therefore 3 : 4′-bromoquinoline. A *tribromoquinoline* melting at 169° (uncorr.) is obtained at the same time.

3 : 4′-*Dibromoquinoline* crystallises from alcohol in lustrous, silky needles melting at 130° (uncorr.). The *hydrochloride* forms colourless, four-sided prisms melting at 185°, and easily decomposed by water, alcohol, or dilute acids. The *nitrate* forms colourless needles and prisms which melt at 158°. The *platinochloride* and the *methiodide* are described.

Generally speaking, whenever a bromoquinoline, with the bromine in the benzene-ring, is brominated, the new bromine-atom enters into the 4′-position; this is the case with anabromoquinoline, the 4 : 4′-dibromoquinoline, previously described by Claus and Decker (Abstr., 1889, 729), being obtained. 4 : 4′-Dibromoquinoline hydrochloride forms lustrous, rhombic tables melting at 183° (uncorr.) and decomposed by water; the nitrate crystallises in colourless, four-sided tables

melting at 147° (uncorr.). The *sulphate*, the *methiodide*, and the *methochloride* and its *platinochloride* are described.

2 : 4′-*Dibromoquinoline*, obtained by heating metabromoquinoline dibromide hydrobromide, crystallises from alcohol in beautiful, thick, colourless rhombohedra which are strongly refractive whilst immersed in the liquid. It melts at 126—127° (uncorr.). The *hydrochloride* is very sparingly soluble; the *nitrate* forms colourless prisms melting at 178°; the *platinochloride* is described; the *methiodide* forms microscopic needles melting at 271° (uncorr.).

1 : 4′-bromoquinoline has been described by Claus and Tornier (Abstr., 1888, 164). A. G. B.

Kynurin. By Z. H. Skraup (*Monatsh.*, **10**, 726—731).—Kynurin, an oxidation-product of cinchonine and of cinchonidine, but not of quinine, is obtained to the extent of about 10 per cent. of the weight of the cinchonic acid taken, when the latter (50 grams) is oxidised with a mixture of chromic acid (20 grams) and sulphuric acid (30 grams) dissolved in water (200 grams). The kynurin (hydroxyquinoline) thus prepared melts at 201°, and has all the properties of the compound obtained by the direct oxidation of cinchonine. On heating at 100—110° with $1\frac{1}{2}$ times its weight of phosphorus pentachloride, it is converted into a chloroquinoline, which melts at 34°, and is reconverted into kynurin by heating with acidified water at 120°; consequently it cannot be α-chloroquinoline, since that compound melts at 38°, and is converted into carbostyril on heating with water. G. T. M.

Alkyl-derivatives of 1-Hydroxyquinoline. By E. Lippmann and F. Fleissner (*Monatsh.*, **10**, 665, 672).—A molecular compound of methoxyquinoline hydriodide and hydroxyquinoline methiodide, $C_9NH_6{\cdot}OMe,HI + C_9NH_6{\cdot}OH,MeI + 2H_2O$ [OH = 1; OMe = 1], is obtained by heating together in sealed tubes at 100° for several hours a mixture of 1-hydroxyquinoline and methyl iodide in molecular proportion, with methyl alcohol. It is insoluble in ether, but soluble in alcohol and water, crystallising from the former in yellow, triclinic plates, decomposes at 143°, gives a hydrochloride, $C_9NH_6MeO,HCl + C_9NH_7O,MeCl + 5H_2O$, forming minute, red crystals easily soluble in water, and a platinochloride, $C_{20}H_{18}N_2O_2,H_2PtCl_6 + 2H_2O$, crystallising in orange-red prisms which decompose at 248°.

Methoxyquinoline-hydroxyquinoline methiodide, $C_{20}H_{19}N_2O_2I$, may be prepared by treating the above compound with ammonia or soda. It crystallises from hot alcohol in orange-red needles, and combines with methyl iodide to form the compound $C_{21}H_{22}N_2O_2I_2 + 2H_2O$, which crystallises in yellow needles and is converted by silver oxide into the deliquescent compound $C_{20}H_{20}N_2O_3$. The iodide, $C_{20}H_{19}N_2O_2I$, on reduction with tin and hydrochloric acid, was expected to yield kairin and tetrahydroxymethoxyquinoline, but only the formation of the former of these compounds could be ascertained. The ethyl-compound, $C_{22}H_{23}N_2O_2I$, is prepared by a method similar to that used in the case of the methyl-compound above described. It crystallises in red

needles which melt at 202°, and furnishes a platinochloride which crystallises with 2 mols. H_2O. G. T. M.

Quinolineparamethenylamidoxime and its Derivatives. By J. Biedermann (*Ber.*, **22**, 2761—2767).—*Quinolineparamethenylamidoxime*, $C_9NH_6{\cdot}C(NH_2){:}NOH$, is formed when paracyanoquinoline (m. p. 135°), prepared from paraquinolinesulphonic acid by Fischer and Willmack's method (Abstr., 1884, 1051), is treated with hydroxylamine hydrochloride and sodium carbonate in dilute alcoholic solution. It crystallises from boiling alcohol in yellowish needles, melts at 105°, and is readily soluble in alcohol and ether, more sparingly in benzene, chloroform, and hot water, and almost insoluble in light petroleum. It dissolves freely in acids, but is only sparingly soluble in alkalis; it gives a greyish-green precipitate with Fehling's solution, and a deep-red coloration with ferric chloride. In aqueous solutions, silver nitrate produces a colourless, crystalline precipitate which darkens after some time with separation of silver. The *hydrochloride*, $C_{10}H_9N_3O,HCl$, crystallises in colourless needles, and is readily soluble in alcohol and water, but insoluble in ether, benzene, light petroleum, and chloroform. The *platinochloride*,

$$(C_{10}H_9N_3O)_2,H_2PtCl_6,$$

crystallises in well-defined prisms. The *ethyl*-derivative, $C_{12}H_{13}N_3O$, crystallises from dilute alcohol in colourless needles, melts at 85°, and is readily soluble in alcohol, ether, chloroform, benzene, and hot water, but almost insoluble in cold water. The *acetyl*-derivative, $C_{12}H_{11}N_3O_2$, prepared by treating the amidoxime with acetic chloride in ethereal solution, crystallises from hot benzene in colourless needles, melts at 115°, and is sparingly soluble in alcohol, ether, chloroform, and benzene, and almost insoluble in cold water.

Quinolineparamethenylethenylazoxime, $C_9NH_6{\cdot}C{<}^{N\cdot O}_{\overline{\ \ N\ \ }}{>}CMe$, prepared by dissolving the amidoxime in hot acetic anhydride, or by digesting the acetyl-derivative with alkalis or water, crystallises from dilute alcohol in slender needles, melts at 175°, and is soluble in alcohol, ether, benzene, and chloroform, but almost insoluble in water. It gives with ferric chloride a bluish-violet coloration, and mercuric chloride and auric chloride produce precipitates in a hydrochloric acid solution.

Ethyl quinolineparamethenylamidoximecarboxylate,

$$C_9NH_6{\cdot}C(NH_2){:}NO{\cdot}COOEt,$$

is formed when the amidoxime is treated with ethyl chlorocarbonate in chloroform solution. It crystallises from boiling alcohol in colourless needles, melts at 97°, and is soluble in ether, chloroform, benzene, and acids, but almost insoluble in light petroleum and cold water, and insoluble in alkalis.

Quinolineparamethenylcarbonylamidoxime, $C_9NH_6{\cdot}C{<}^{N\cdot O}_{NH}{>}CO$, prepared by boiling the preceding compound with alkalis, or by digesting the amidoxime with excess of ethyl chlorocarbonate, crystallises from

boiling benzene in colourless needles, melts at 155°, and is soluble in alcohol, ether, chloroform, and alkalis, but almost insoluble in cold water. In aqueous solutions of the ammonium-derivative, copper sulphate produces a green, lead acetate and silver nitrate a colourless, crystalline precipitate.

Quinolineparamethenyluramidoxime, $C_9NH_6 \cdot C(NOH) \cdot NH \cdot CONH_2$, separates in colourless crystals when a concentrated, aqueous solution of the amidoxime hydrochloride is treated with potassium cyanate; it crystallises from boiling water in small, colourless needles, melts at 164·5°, and is only sparingly soluble in cold water and acids, but more readily in hot water, alcohol, ether, benzene, light petroleum, and alkalis.

Quinolineparamethenylbenzenylazoximeparacarboxylic acid,

$$C_9NH_6 \cdot C \begin{matrix} \nearrow N \cdot O \searrow \\ \searrow \text{—} N \nearrow \end{matrix} C \cdot C_6H_4 \cdot COOH,$$

prepared by melting the amidoxime with phthalic anhydride, crystallises from hot alcohol in colourless needles, melts at 203°, and is soluble in ether and chloroform, but only sparingly in benzene and water, and almost insoluble in light petroleum. F. S. K.

α-Cinnamenylcinchonic Acid and 2:4-Quinolinedicarboxylic Acid. By O. Doebner and J. Peters (*Ber.*, **22**, 3006—3011).—*α-Cinnamenylcinchonic acid*, $CHPh\colon CH \cdot C \begin{matrix} \nearrow N\text{—}C_6H_4 \\ \searrow CH\colon C \cdot COOH \end{matrix}$, is prepared by gradually adding from a dropping funnel an alcoholic solution of aniline (52 grams) to a solution of cinnamaldehyde (75 grams) and pyruvic acid (50 grams) in absolute alcohol. The whole is boiled in a reflux apparatus on a water-bath for four to five hours; the liquid is then concentrated, and the crystals which separate washed with ether and crystallised from hot alcohol. The yield is 10 grams. The acid crystallises in yellow needles, melts at 295° with evolution of carbonic anhydride, is insoluble in water, sparingly soluble in ether, benzene, and chloroform, more soluble in hot alcohol, especially if a few drops of hydrochloric acid are added. The acid solution has a green fluorescence. The *potassium*, *sodium*, and *ammonium salts* are readily soluble; the *magnesium salt*, $(C_{18}H_{12}NO_2)_2Mg$, crystallises in concentrically-grouped, lustrous, yellow needles; the *silver salt* is a flaky precipitate; the *nickel* and *copper salts* are yellowish-green, and the *zinc* and *lead* salts yellow. When the acid is distilled, it decomposes into benzylidenequinaldine (Jacobsen and Reimen, Abstr., 1884, 335) and carbonic anhydride.

Cinnamenylcinchonic acid is also formed by heating α-methylcinchonic acid with benzaldehyde and zinc chloride, and by the action of aniline on pyruvic acid and cinnamaldehyde at the ordinary temperature. In the latter case an indifferent compound of the formula $C_{24}H_{20}N_2O$ is obtained, which crystallises from glacial acetic acid in yellowish needles melting at 194°.

2 : 4-*Quinolinedicarboxylic acid*, $C_9NH_5(COOH)_2$, is obtained by adding a solution of potassium permanganate (7·5 grams) in water (500 c.c.) to a solution of α-cinnamenylcinchonic acid in

soda diluted to 500 c.c. After 24 hours it is filtered, evaporated down to one-third of its bulk, treated with dilute hydrochloric acid, and allowed to cool. The acid separates in slender needles, and is crystallised from water. It melts at 246° with decomposition, is sparingly soluble in cold water, alcohol, and ether, insoluble in benzene and chloroform. The *calcium salt*, $C_{11}H_5NO_4Ca$, crystallises in slender, white, lustrous needles; the *barium salt* forms groups of long needles; the *copper salt* (with 1 mol. H_2O) is a sparingly soluble, bluish-green precipitate; the *silver salt* is a very gelatinous, white precipitate: other salts were prepared. When the acid is heated above its melting point, it partly sublimes, and is partly decomposed into quinoline and carbonic anhydride. N. H. M.

Hydroquinoline-derivatives. By O. SRPEK (*Monatsh.*, **10**, 701—729).—A solution of the hydrochloride of quinic acid (20 grams) in concentrated hydrochloric acid (100 grams) was mixed with stannous chloride (10 grams), and then heated with metallic tin (28 grams). When the metal had dissolved, the solution was saturated with hydrogen sulphide to precipitate the tin, filtered, and concentrated in an atmosphere of carbonic anhydride, whereby the hydrochloride of *tetrahydroquininic acid*, $C_{11}H_{13}NO_3,HCl$, crystallising in small needles melting at 205—206° (uncorr.), separated out. The acid has probably all four, but certainly two, hydrogen-atoms attached to the pyridine nucleus, since it gives an acetyl-derivative, $C_{11}H_{12}AcNO_3$, melting at 240—241° (uncorr.), and, therefore, contains an imidogen-group. On treatment with bromine, the acid furnishes what is probably an additive product, which has a red colour, and on treating this with hot hydrochloric acid, washing with water, boiling with sodium hydrogen sulphite, and recrystallising from xylene, it gives tribromoquinanisoïl, $C_{10}H_6Br_3NO$, a substance which crystallises in white needles, melts at 233°, and is identical with the compound obtained by Skraup from thalline; on heating it with concentrated hydrochloric acid, first at 150° and afterwards at 170°—180°, it gives a *tribromhydroxyquinoline*. This tribromhydroxyquinoline crystallises from acetic acid in needles melting at 218° (uncorr.), and is also produced, together with tribromoquinanisoïl, on bromination of thalline hydrochloride.

Tribromoquinanisoïl is oxidised by boiling concentrated nitric acid to a *bromopyridinecarboxylic acid* which melts at 182° (uncorr.), and proves to be identical with the bromonicotinic acid obtained by Claus and Collishonn (Abstr., 1887, 158). Tribromohydroxyquinoline is converted by potassium permanganate into a *bromoquinolinic acid*, $C_5H_2Br(COOH)_2 + H_2O$, which appears to be identical with the acid obtained by Claus and Collishonn (*loc. cit.*), and decomposes at 165° into carbonic anhydride and the above-mentioned bromonicotinic acid. On fusion with potash, these bromonicotinic acids furnish an acid free from bromine and 4′-hydroxypyridine. The tribromo-compounds must consequently be regarded as having one bromine-atom in the 4′-position of the pyridine nucleus, and the other two atoms in the benzene nucleus.

Tetrahydrobromhydroxyquinoline hydrochloride, $C_9NH_9Br{\cdot}OH,HCl$,

which crystallises in needles melting at 238°, is obtained on reducing tribromohydroxyquinoline with tin and hydrochloric acid.

G. T. M.

Formation of Azines from Orthodiamines and Polyamines. By R. NIETZKI (*Ber.*, 22, 3039—3040).—A discussion of the bearing of recent work on this subject.

Derivatives of Orthamidobenzyl Alcohol. By H. G. SÖDERBAUM and O. WIDMAN (*Ber.*, 22, 2933—2942).—The *platinochloride* of the benzophenyldihydroketometadiazine previously described (Abstr., 1889, 973) forms prismatic crystals melting with decomposition at 199°; the *aurochloride*, yellow needles melting at 170—172°.

Phenomethyldihydrothiometadiazine, $C_6H_4<\begin{matrix}CH_2\cdot NMe\\ NH\cdot CS\end{matrix}$, is formed by heating orthamidobenzyl alcohol with methyl thiocyanate in benzene solution. *Hydroxytolylmethylthiocarbamide* is first formed as a brown oil, which becomes thick on cooling but does not crystallise, and if this is heated with hydrochloric acid, it is converted into the diazine, which crystallises from methyl alcohol in long, glistening needles and melts at 139°. The *platinochloride* crystallises in four-sided plates melting with decomposition at 195°; the *aurochloride* forms yellow, microscopic needles melting at 151—153°.

ω-Hydroxytolylethylthiocarbamide, formed like its methyl analogue, is also an oil, and with hydrochloric acid yields *phenethyldihydrothiometadiazine*, $C_6H_4<\begin{matrix}CH_2\cdot NEt\\ NH\cdot CS\end{matrix}$, which crystallises from alcohol in long needles melting at 103°. The *platinochloride* is a pale-yellow powder melting at 208°; the *aurochloride* forms crystals melting at 118°.

When the methylthiocarbamide is heated with mercuric oxide, it yields *phenomethyldihydroketometadiazine*, $C_6H_4<\begin{matrix}CH_2\cdot NMe\\ NH\cdot CO\end{matrix}$. This is easily soluble in organic solvents, sparingly so in water. The *platinochloride*, $(C_9H_{10}N_2O)_2,H_2PtCl_6$, crystallises in needles or plates melting at 202—203°, the aurochloride, $(C_9H_{10}N_2O),HAuCl_4$, in yellow, glistening prisms melting at 185°. The ethylthiocarbamide in like manner yields *phenethyldihydroketometadiazine*, which crystallises from alcohol in flat, colourless needles and melts at 94—95°. The *platinochloride* crystallises in yellow needles melting with decomposition at 205°; the *aurochloride* forms golden-yellow scales melting at 116—118°.

Phenallyldihydroketometadiazine, $C_6H_4<\begin{matrix}CH_2\cdot N\cdot C_3H_5\\ NH\cdot CO\end{matrix}$, prepared from the allylthiocarbamide, is very soluble in alcohol, crystallises in microscopic prisms, and melts at 77—78°. The *platinochloride* crystallises in needles and melts at 169—171°.

Benzophenodihydroketometadiazine, $C_6H_4<\begin{matrix}CH_2\cdot NPh\\ NH\cdot CO\end{matrix}$, prepared from the benzothiocarbamide, crystallises from alcohol in needles or prisms melting at 145—146°. It forms a crystalline platinochloride and aurochloride. All attempts to obtain phenodihydrothiodiazine proved

futile. The author points out the regularity of the melting points in these thio- and oxy-series.

When oxidised with chromic acid in acetic acid solution, phenodihydroketometadiazine yields benzoylencarbamide, $C_6H_4<\begin{matrix}CO\cdot NH\\ NH\cdot CO\end{matrix}$, described by Griess and by Abt.

The formation of these two groups of compounds appears at first sight to be analogous to that of the pseudo-carbamides lately described by Gabriel (Abstr., 1889, 848). But after a careful examination of the evidence the author concludes that the formulæ ascribed by him to the diazine is correct, and that his and Gabriel's compounds are not strictly analogous.
L. T. T.

Codeïne Methiodide. By Z. H. SKRAUP and D. WIEGMANN (*Monatsh.*, **10**, 732—733). It has been previously shown (Abstr., 1889, 1018) that in all probability the nitrogen-atom in morphine has both a methyl- and an ethyl-group directly attached to it. If this view is a correct one, codeïne methiodide, which on heating with alkalis is converted into methylmorphemethine, should give rise to ethyldimethylamine when treated with alcoholic potash, and not to dimetbylamine (the product said to be obtained by Knorr, Abstr., 1889, 417). On repeating Knorr's experiments, the authors find that ethyldimethylamine, together with a small quantity of trimethylamine, is really produced, and furnishes a characteristic platinochloride, which is sparingly soluble with alcohol, and crystallises from water in octahedra melting at 193°.
G. T. M.

Oxidation-products of Quinoidine. By H. STRACHE (*Monatsh.*, **10**, 642—646; compare Abstr., 1889, 1016).—When quinoidine (800 grams) is oxidised by boiling with commercial nitric acid (about 26 kilos.), added a little at a time until the solution is no longer rendered turbid by ammonia, a mixture of α-pyridinetricarboxylic acid (73 grams), cinchomeronic acid (48 grams of the hydrochloride), and cinchonic acid (34 grams) is obtained. At the same time a hydrochloride of a nitroquinolinecarboxylic acid is formed, which on sublimation gives a nitroquinoline crystallising in needles melting at 153—154°. The properties of this base agree with those of La Coste's 4-nitroquinoline.
G. T. M.

Action of Potash on Alkyl Halogen-derivatives of Papaverine. By G. GOLDSCHMIEDT (*Monatsh.*, **10**, 673—691).—The author defends the views of Stransky (Abstr., 1889, 166) against those of Claus and Edinger (*ibid.*, 415), and has made the following observations on repeating Stransky's experiments. According to Claus, the bases obtained on treating the alkyl halogen additive products of papaverine with silver oxide and with potash respectively, differ considerably, for whereas the hydrochloride and alkyl chlorides of the former give a platinochloride which is crystalline, anhydrous, and may be crystallised from hot water, the hydrochloride of the latter gives a platinochloride containing water of crystallisation, and which readily decomposes when attempts are made to recrystallise it from

boiling water. Claus and Edinger obtained from the methyl base an uncrystallisable platinochloride, containing 1 mol. H_2O, and Hütlein found that the ethyl base gave a crystalline platinochloride, also containing 1 mol. H_2O. The author shows that the platinochloride of ethylpapaverinium oxide $(C_{20}H_{21}NO_4Et)_2PtCl_6 + 3\frac{1}{2}H_2O$, prepared by means of potash, and the corresponding methyl-compound,

$$(C_{20}H_{21}NO_4Me)_2PtCl_6 + 3H_2O,$$

similarly prepared, are both stable in presence of boiling water, whilst the methyl-compound, obtained by means of silver oxide, is an anhydrous salt. On the other hand, the hydrobromide obtained by Stransky from ethylpapaverinium oxide and hydrobromic acid is crystallographically identical with the papaverine ethyl bromide previously described by the author. Of these apparently contradictory facts no explanation can at present be offered.

Claus and Hütlein have expressed the opinion that during the action of potash on the alkyl halogen-derivatives of papaverine, the alkyl-groups swing from the nitrogen- to a carbon-atom; the author, however, finds that ethylamine is formed by boiling papaverine ethyl bromide with potash; at the same time, a compound melting at 240°, and also one melting at 186—187°, crystallising from alcohol in white needles, having the formula $C_{19}H_{20}O_5$ or $C_{19}H_{18}O_5$, and containing four methoxyl-groups, are formed. G. T. M.

Papaverinic and Pyropapaverinic Acids. By G. GOLDSCHMIEDT and H. STRACHE (*Monatsh.*, **10**, 692—700; compare Abstr., 1888, 302).—Correcting a previous communication (Abstr., 1886, 479), the authors state that papaverinic acid (Abstr., 1885, 1080), $C_{16}H_{13}NO_7$, crystallises with 1 mol. H_2O, and furnishes a ketoxime, $C_{16}H_{14}N_2O_7$, which crystallises from alcohol in small needles melting at 154—157°.

Ammonium pyropapaverinate gives precipitates with many metallic salts, and may be used to prepare the undermentioned compounds: Calcium pyropapaverinate, $(C_{15}H_{12}NO_5)_2Ca + 4H_2O$, crystallises in groups of needles; barium pyropapaverinate, $(C_{15}H_{12}NO_5)_2Ba + 4H_2O$, in plates; the hydrochloride, $C_{15}H_{13}NO_5,HCl + H_2O$, crystallises in orange-red needles; the phenylhydrazone, $C_{15}H_{13}NO_4{:}N_2HPh$, crystallises from alcohol in yellow prisms, softens and turns red at 210°, melts with decomposition at 223°, and forms a hydrochloride,

$$C_{15}H_{13}NO_4{:}N_2HPh,HCl,$$

a vermilion-coloured powder. The ketoxime of pyropapaverinic acid, $C_{15}H_{14}N_2O_5$, crystallises from alcohol in needles melting at 226°, its hydrochloride, $C_{15}H_{14}N_2O_5,HCl + H_2O$, crystallises in lemon-yellow needles, which lose HCl and H_2O when heated at 105°, and are slowly decomposed on boiling with water. G. T. M.

Ulexine. By A. W. GERRARD and W. H. SYMONS (*Pharm. J. Trans.* [3], **19**, 1029—1030).—Ulexine, $C_{11}H_{14}N_2O$, the alkaloïd previously obtained by the authors from the seeds of the common furze, *Ulex Europæus* (Abstr., 1886, 1048), forms colourless, odourless, deliquescent crystals, freely soluble in chloroform, but insoluble in

absolute ether. The substance fuses at 151°, and begins to char at 175°. It cannot be sublimed without decomposition. It is a strong base, for it precipitates quinine, cocaïne, and strychnine, and also liberates ammonia from its compounds. The platinochloride,

$$(C_{11}H_{14}N_2O)_2,H_2PtCl_6,$$

forms lustrous, crystalline plates; the aurochloride, $C_{11}H_{14}N_2O,HAuCl_4$, was also analysed.

When ulexine is treated with alkaline permanganate, it gives off two-thirds of its nitrogen as ammonia. Ulexine has a powerful physiological action, and one-tenth of a grain has been found to produce toxic effects. It raises arterial tension, produces diuresis, and acts as a nerve and muscle poison, affecting the respiratory organs especially.

A second base seems also to occur in the seeds, but has not yet been obtained in quantity sufficient for examination. R. R.

Bile-Pigments. By J. B. HAYCRAFT and H. SCOFIELD (*Zeit. physiol. Chem.*, **14**, 173—181).—When bilirubin is oxidised, biliverdin is formed; if the oxidation be carried further, as by nitric acid, a blue pigment, bilicyanin, is formed, then a violet (perhaps a mixture of the blue and red), then a red, and lastly a yellow pigment (choletelin) are formed. There have been, however, very few experiments recorded in which by means of reducing agents the lower terms of the series have been obtained from the higher. Lauder Brunton (*Handb. of Physiol. Lab.*, p. 498) alone mentions that sulphuric acid colours an alkaline solution of biliverdin yellow, and that if this yellow solution is then treated with nitric acid, a solution of bilirubin is obtained.

In the present research it was noticed that ox bile, on being allowed to remain for some hours, changed in colour from green to orange-brown. This is regarded as reduction, for if nitric acid be added to it, bilirubin is first obtained, and then the usual series of green, blue, violet, red, and yellow pigments. It was also noticed that the bile in the gall-bladder was yellowish where it came in contact with the wall of that viscus; this is an instance of reduction brought about by living tissues. Another instance of reduction is the presence of gall-stones, coloured by bilirubin in the bile of the ox, of which the natural pigment is biliverdin.

Experiments were then carefully performed in which bile was observed under different conditions in the air, in closed sterilised tubes, mixed with pieces of mucous membrane and so forth, from which the following conclusions are drawn:—That biliverdin parts with its oxygen as easily as oxyhæmoglobin; in sterilised vessels the reduction stops at bilirubin; the reduction is hastened by exposure to light, putrefaction, and admixture with mucus or mucous membrane, but hindered by darkness and drying the bile. When putrefaction occurs, reduction goes on to the formation of a brownish pigment, which gives no play of colours with Gmelin's test, but which differs from hydrobilirubin by being insoluble in ether, and easily soluble in alcohol. It moreover shows no absorption-bands. Copeman and Winston (Abstr., 1889, 792) have observed that human bile is olive-

green; probably this undergoes reduction after death; hence the pigment usually described in human bile is bilirubin.

The play of colours can be obtained at the positive pole of a battery (4 Grove cells) placed in the bile, indicating successive stages of oxidation; if the negative pole be then placed in the bile, the series is reversed, indicating reduction. W. D. H.

Preparation of Crystalline Egg-albumin. By F. HOFMEISTER (*Zeit. physiol. Chem.*, **14**, 165—172).—Fresh white of egg freed from membranes was mixed with an equal volume of saturated solution of ammouium sulphate to precipitate the globulin, and the filtrate allowed to evaporate in flat dishes at the ordinary temperature. In a few days a deposit of granules or scaly aggregations of granules was observed, and later needles or stellate collections of needles were mixed with these. Whether these are pure egg-albumin or a compound of egg-albumin with ammonium sulphate, and whether other animal proteïds act similarly, are questions which have still to be investigated. Remarks on the differences between colloïds and crystalloïds, and the necessity of modifying our ideas concerning this difference, conclude the paper. W. D. H.

Peptone and Similar Substances. By J. SEBELIEN (*Bied. Centr.*, 1889, 717—718).—Pure milk caseïn was digested with peptone and hydrochloric acid, the nucleïn filtered off, all albumoses separated by ammonium sulphate, and the resulting filtrate mixed with tannin. The precipitate thus obtained was decomposed by baryta-water, and then the barium removed. A solution of pure peptone was thus obtained, and was only precipitated by alcohol, phosphotungstic acid, and tannin, and was redissolved by excess of the latter. Optical estimation of the amount of peptone present indicated a percentage of only 1·2—2·7 per cent., which was obviously too low; hence it was concluded that the compound was almost, or even quite, inactive. E. W. P.

Physiological Chemistry.

Calorimetric Investigations on Heat Production in Animals. By J. ROSENTHAL (*Arch. Anat. Physiol., physiol, Abth.*, 1889, 1—53). —A long account of investigations relating chiefly to the influence of body weight and food on the production of heat, together with full descriptions of the methods employed, including that of the air-calorimeter. W. D. H.

Conditions of Absorption of various Hæmoglobins. By S. JOLIN (*Arch. Anat. Physiol,, physiol. Abth.*, 1889, 265—288).—Böhr (*Ludwig's Festschrift*, 1886) has shown in experiments with the hæmoglobin of the dog, by the use of a new absorptiometric method, how the dissociable unions of hæmoglobin with oxygen and with car-

bonic anhydride vary with differences of pressure. This is not strictly proportional to the pressure, but falls at first slowly, but with low pressures (below 20 or 30 mm. of mercury) very quickly. This can be represented graphically by a curve constructed from abscissæ representing the pressure, and ordinates representing the amount of gas absorbed by 1 gram of hæmoglobin; the curve so obtained with oxygen is quite different from that obtained with carbonic anhydride.

In the present research, the same methods were applied first to guinea-pig's hæmoglobin, which crystallises in rhombic tetrahedra, not in prisms, as dog's hæmoglobin does; and secondly with goose's hæmoglobin, as an instance of blood pigment occurring in nucleated red corpuscles. In the first case, the results obtained were practically the same as in Böhr's researches, the difference of crystalline form causing no difference in the type of the curves produced, the general conclusion being that there are two possible compounds of each of the gases with the hæmoglobin. With regard to the second series of experiments, those with birds' hæmoglobin, the curves are in respect to both gases of a character different from those obtained with mammalian blood pigment. The curves are flatter, and show that the quantity of gas absorbed in the first place is less, and in the second place does not increase with the pressure beyond a certain point, namely, 95 mm. in the case of oxygen, 65 mm. in that of carbonic anhydride.

W. D. H.

Gases in the Swimming-bladder of Fishes. By M. TRAUBE-MENGARINI (*Arch. Anat. Physiol., physiol. Abth.*, 1889, 54—63).—If fish are placed in water containing hydrogen in solution, the swimming-bladder, whether it be of the open or closed variety, becomes in a few hours filled or partially so with the gas. This fact shows that the gases of the swimming-bladder are more or less directly obtained from water in which the fish is living. W. D. H.

Digestion in the Pig. By ELLENBERGER and HOFMEISTER (*Arch. Anat. Physiol., physiol. Abth.*, 1889, 137—153).—This is an account of experiments on the pig carried out on the same lines as previous experiments by the same authors on other animals. The anatomy of the stomach, the process of digestion with different foods in different parts of the alimentary canal, and the process of absorption are described. With regard to gastric digestion, an important point made out is that the proteolytic period is preceded by a period in which no secretion of acid takes place, and when amylolytic action proceeds freely. W. D. H.

Absorption of Fat in the Intestine. By A. GRUENHAGEN and KROHN (*Bied. Centr.*, **18**, 617—619; from *Arch. Phys.*, **24**, 535—545). —The author showed some time ago that the epithelium cells of the intestine cut out of a frog, as well as those in the living organism, are capable of taking up drops of fat from the intestinal tube filled with fat or emulsion.

The experiments were made with frogs which had not been fed for

some time, so that the intestine should be free from food constituents. The substances employed were milk, olive oil, lanolin emulsion, and, to determine whether the epithelium absorption is confined to fatty substances (Funke's view), a solution (?) of the finest Chinese ink. The results of the experiments show that the assumption of a mechanical activity of the epithelium of the intestines in taking up of fat is inadmissible, inasmuch as only fat and not even the finest grains of other substances enter into the protoplasma of the border cells. It is also established that the intestinal epithelium of hibernating frogs forms a store place for excess of fat, and will retain fatty substances enclosed in it with great tenacity. N. H. M.

Origin of Urea in the Animal Economy. By F. COPPOLA (*Chem. Centr.*, 1889, ii, 375; from *Rend. Acad. dei Lincei* [4], **5**, 1).—A dog was fed with an insufficient amount of bread for a month, at the end of which time its weight remained constant. The urea and acidity were determined in the voidings for five days, and then varying quantities of cyanuric acid were administered in addition to the daily ration of bread, the urea and acidity being still determined. The administration of the cyanuric acid had no influence on the weight of the animal. Up to 1 gram of administered cyanuric acid, the amount of urea increased; an excess of this amount had no further influence on the quantity of urea formed. Some of the cyanuric acid passed away with the excreta, and the total acidity increased with the amount of cyanuric acid administered. The author concludes that one part of the cyanuric acid is changed into carbimide, which is further decomposed into water and carbonic anhydride, the ammonia then combining with a second portion of cyanuric acid, with formation of urea. J. W. L.

Origin of Uric Acid in Mammals. By J. HORBACZEWSKI (*Monatsh.*, **10**, 624—641).—Since uric acid is a derivative of acrylic acid, and is produced in abnormally large quantities when glycerol is taken internally, it was thought probable that it might be built up synthetically in mammals from acrylic acid, and some nitrogenous compound, such as urea. In order to ascertain whether this was the case, sodium acrylate was mixed with the food of a strictly dieted subject, but no increase in the quantity of uric acid formed could be observed. The urine, however, showed indications of becoming alkaline, a result probably due to the formation of sodium carbonate from the sodium acrylate.

Minkovski has suggested (*Arch. exper. Path. Pharm.*, **21**) that in birds the formation of uric acid is probably due to some function of the liver, whereby the acid is built up from lactic acid and ammonia, but the author now shows that in the case of men whose death results from *cirrhosis hepatis*, the amount of uric acid formed does not vary with the progress of the disease, and that mixtures of fresh spleenic juice and defibrinated blood, obtained from recently-killed calves, through which, at 37—40°, a slow stream of air is passed, give rise to very considerable quantities of uric acid. This result is not produced by the blood alone, and must be regarded as due to a function of the

spleen, which perhaps under some circumstances brings about the degradation of the white corpuscles of the blood. G. T. M.

Changes in the Glycogen, Sugar, and Lactic Acid of the Muscle while performing Work. By A. MOLINARI (*Chem. Centr.*, 1889, ii, 372—373, from *Ann. Chim. Farm.*, 9, 351—366).—The muscles of two dogs, one of which had rested and weighed 20·5 kilos., whilst the other had run 92 kilometres (57 miles) and weighed 25·5 kilos., were analysed, and the respective amounts of glycogen, sugar, and lactic acid determined. The glycogen was estimated by Windgradoff's method.

In the filtrate from the precipitated glycogen, the sugar was determined by Fehling's solution. The lactic acid was estimated by two methods. By the first, 350 grams of muscle is extracted with water, concentrated somewhat, 99 per cent. alcohol added, the filtrate distilled aud concentrated, and the residual alcohol-free liquid diluted with a little water. A slight excess of lead acetate is added, the filtrate and washing concentrated in order to allow the creatine to crystallise out, the mother-liquor acidified and extracted with ether, the ether distilled off, the residue dissolved in a little water, powdered zinc oxide added, the filtrate again concentrated, and treated with four or five volumes of 99 per cent. alcohol, and the precipitate filtered off, dried, and weighed. In the second method, baryta is used to remove the phosphates. The results obtained by the two different methods did not agree very closely, and the author recommends the former as the more exact.

In the muscles of the tired dog, less glycogen and lactic acid but more sugar was found, showing that the lactic acid is not formed from the glycogen. J. W. L.

Diastatic Ferment of the Liver. By KAUFMANN (*Compt. rend. Soc. Biol.* [9], 1, 600—603).—Bernard first advanced the doctrine that the hepatic glycogen is transformed into sugar by a ferment which is separable from the liver substance. Recent observations by Dastre (and others not quoted) have thrown doubt on the existence of such a special ferment. In the present research, it was sought to further elucidate the question by examining the secretion of the liver, not the liver substance itself. Dog's bile was found to be free from a saccharifying ferment. Cat's bile was feebly saccharifying. The bile of the pig, sheep, and ox was found to be powerful in converting starch into sugar. These facts are considered as additional evidence that a diastatic ferment is formed by the liver; the dog, however, is supposed to transform its glycogen into sugar by some other means.
W. D. H.

Quantity of Iron in the Spleen and Liver of Young Animals. By L. LAPICQUE (*Compt. rend. Soc. Biol.* [9], 1, 510—512).—The spleen of young animals is poor in iron. Four rabbits born at the same time were taken. Intravenous injection of distilled water was performed on two of these in order to destroy some of their red-blood corpuscles; their spleens contained respectively 0·24 and 0·26 parts of iron per 1000; the amount of iron in the spleens of the other

two animals, which served as control specimens, was 0·44 and 0·19 per 1000 respectively. The result is thus an uncertain one.

Estimations were then made to determine if the quantity of iron in the liver varies with age. The organs were in each case freed from blood, and the results were as follows :—

Age of rabbit.	Weight in kilos.	Parts of iron per 1000.	
		In blood.	In liver.
8 days	0·120	0·45	1·00
11 days	0·137	0·40	0·20
21 days	0·320	0·41	0·14
3 months	1·170	—	0·043
3 months	1·350	0·42	0·035
3 months	1·360	0·36	0·040

The quantity of iron thus diminishes with the age of the animal.

W. D. H.

The Physiological Rôle of Lactose. By A. DASTRE (*Compt. rend. Soc. Biol.* [9], 1, 145—149).—Although lactose is so important as a food, it is stated that very little is known of the part it plays in the organism. The present communication relates to the question whether lactose is itself assimilable. The conclusion arrived at is that which others have found before, that lactose is not directly assimilable, but is first inverted in the alimentary canal. What agent accomplishes this change is still uncertain. After injecting into the circulation a mixture of galactose and glucose, a small quantity of the sugar which is not utilised passes into the urine. This sugar is a reducing one, but does not undergo the alcoholic fermentation. Its nature is, however, uncertain.

W. D. H.

Physiology of the Tannins. By F. REINITZER (*Chem. Centr.*, 1889, ii, 292—293, from *Ber. deut. bot. Gesell.*, **7**, 187—196).—The author contends that the assertion of Kraus (Abstr., 1889, 917), that the tannins of various origins are physiologically alike, is not correct, and that the methods at present employed for the determination of tannin are not suitable for physiological investigation, however useful they may be for the practical valuation by the tanner.

J. W. L.

Volatile Fatty Acids of Butter. By P. SPALLANZANI (*Chem. Centr.*, 1889, ii, 339—341, from *Staz. sperem. agric. ital.*, **16**, 277—293).—The author has carried out an investigation into the cause of butter fat containing so variable a quantity of volatile fatty acids. Four different breeds of cows, namely, that of the Province Reggio d'Emilia, Dutch, Schwitz, and Simmenthal, were employed and fed exactly in the same way. The cream of the milk of the several different breeds was separately churned, as was also cream which was 12 hours, and that which was 36 hours old. Further, the influence of length of time from calving, the sudden changing of food, and the

age of the butter, with regard to the quantity of volatile fatty acids in the butter, was investigated.

The amount of volatile fatty acids, expressed in terms of c.c. of decinormal alkali per 5 grams of butter fat, varied from 20·63 to 30·60. Nor could any regularity in the quality of butter obtained from the different sources be observed. The butter from cows stationed at high lying places contained usually more volatile fatty acids than that from low lying stations. Of the different breeds that of Schwitz gave butter containing most fatty acids, then followed the breeds Simmenthal and Reggio, alike in this respect, and last the Dutch. Lastly, with regard to the influence of length of time since calving, the percentage of fatty acids declined as this period advanced.

J. W. L.

Urobilin in the Bile. By J. Winter (*Compt. rend. Soc. Biol.* [9], 1, 139).—In reference to the method adopted by Engel and Kiener (Abstr., 1889, 637) for the separation of urobilin, it is pointed out that the precipitates of the biliary constituents produced by adding calcium salts, especially the phosphate, carry urobilin down with them. The final filtrate, even in urines rich in urobilin, is always colourless. The conclusion drawn by Engel and Kiener, that urobilin is absent from the bile, is therefore not proved, as their method was one unsuited for discovering small quantities of that pigment.

W. D. H.

The Behaviour of Tyrosine Ethyl Ether in Animal Metabolism. By R. Cohn (*Zeit. physiol. Chem.*, **14**, 189—202).—Considering the amount of proteïd daily ingested by an animal, the amount of tyrosine formed cannot be inconsiderable. Blendermann (Abstr., 1883, 876) and Jaffe (*Zeit. physiol. Chem.*, **7**) by feeding animals with tyrosine could, however, find no increase in the aromatic substances in the urine, nor indeed any constant relation between tyrosine or any urinary constituent. Baas (Abstr., 1887, 1133) found no increase in the hippuric acid secreted in similar experiments. In the present experiments on dogs and rabbits, the tyrosine ethyl ether hydrochloride was injected both subcutaneously and intravenously. Large doses acted fatally: but no tyrosine was ever found in the urine or bile; nor was there an increase in aromatic hydroxy-acids, phenol, or hippuric acid. It is thus probable that tyrosine undergoes complete destruction in the organism.

W. D. H.

Determination of Potassium in Urine as Potassium Hydrogen Tartrate. By A. Robin (*Compt. rend. Soc. Biol.* [9], 1, 356—363).—When the potassium in urine is estimated by the weight of the precipitate obtained by adding tartaric acid to concentrated urine, the results obtained as compared with those obtained from the platinic chloride method are found to be from 9 to 70 per cent. too high. All conclusions drawn from such estimations are therefore null. Roger and Gaume have stated that the output of potassium salts is increased in ague and certain other diseases; their conclusions regarding this subject, and also regarding the toxicity of urine from the presence in it of potassium salts, rest on experiments performed by the tartaric

acid method. The precipitate produced by tartaric acid in urine carries down with it uric acid, hippuric acid, albumin, and other organic substances. W. D. H.

Reducing Substances in Urine. By GAUBE (*Compt. rend. Soc. Biol.* [9], 1, 383—390).—Various urines were examined with regard to the substances in them that reduce alkaline solutions of cupric hydroxide. In one case, that of an emaciated child, the reducing substance is stated to have been aldehyde. The following statements are also made:—In acetonæmia and acetonuria, lactic acid exists in the urine, in combination conjointly with phosphoric acid, producing acid salts, principally of potassium, to which the acidity of the urine in these cases is chiefly due. Lactose is said to be met with in the urine of cases of what the author terms oxycrasia. W. D. H.

Benzamide in Urine after Administration of Benzaldehyde. By R. COHN (*Zeit. physiol. Chem.*, **14**, 203—208).—After feeding dogs on benzaldehyde (10 grams per diem), the urine was collected, extracted with hot alcohol, the extracts evaporated, and the deposit dissolved in water strongly acidified with sulphuric acid. This was shaken with ether; the ethereal extracts concentrated, and the hippuric acid so deposited filtered off. The ether was distilled off, and the small crystalline residue was dissolved in a concentrated solution of sodium carbonate, and again shaken with ether; the ether was again evaporated, and the crystalline residue was recrystallised from hot water, animal charcoal being used to decolorise it. The crystals were right-angled plates soluble in water, giving a neutral reaction, sparingly soluble in cold ether and light petroleum, easily in hot ether, in alcohol, and in hot benzene. They melted easily (127—128° uncor.), sublimed without decomposing, and contained no water of crystallisation, and proved to be benzamide; about 4 grams of it were obtained in the urine for every 100 grams of benzaldehyde given to the animal.

In the rabbit no benzamide was found in the urine, even after subcutaneous injection of ammonium benzoate; probably in this animal the ammonia derived from the benzoate is completely used in building up urea. W. D. H.

Uroleucic Acid and Alcaptonuria. By R. KIRK (*Brit. Med. J.*, **2**, 1889, 1149—1150).—Prof. Huppert, in a private communication to the author, regards the uroleucic acid ($C_9H_{10}O_5$) previously described by him (Abstr., 1888, 1121) in the urine of cases of alcaptonuria as a homologue of gallic acid and probably pyrogallolpropionic acid, or at least a trihydroxyphenylpropionic acid, $C_6H_2(HO)_3{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$. It does not give the genuine Millon's reaction, and therefore contains either no hydroxyl-group in the benzene nucleus, or more than one; it is optically inactive, and therefore contains no asymmetrical carbon-atom.

Uroleucic acid was found to have considerable antiseptic power. It is entirely absent in normal urine. The substance previously described as uroxanthic acid, which accompanies uroleucic acid in these peculiar

urines, has been more fully investigated, and found to consist simply of uroleucic acid mixed with hippuric acid as an impurity.

W. D. H.

Cystinuria. By B. MESTER (*Zeit. physiol. Chem.*, **14**, 109—150). —This paper relates to the examination of the urine of patients suffering from cystinuria, and many of the considerations introduced are of clinical, therapeutical, historical, and theoretical interest. The chief points of chemical importance relate to:—

(1.) The solubility of cystin in urine; it appears that even in acid urine as much as 0·5 gram of cystin will dissolve per litre.

(2.) The sulphur in cystin is doubtless combined in a non-oxidised form; numerous analyses in this direction are tabulated; and the average result of estimations on the urine from nine individuals shows that the non-oxidised sulphur forms 18·1 per cent. of the total sulphur; from these numbers a method is devised for estimating the amount of cystin in urine.

(3.) Different kinds of diet, and the use of alcohol, appeared to be without influence on the amount of cystin excreted.

(4.) By administering sulphur and also salol as drugs, the amount of unoxidised sulphur in the urine was practically unchanged.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Colouring Matters and Aromatic Products from the Bacillus Pyocyanicus. By A. BABÈS (*Compt. rend. Soc. Biol.* [9], **1**, 438—440). —A pure culture of the *B. pyocyanicus* β (Ernst) in neutralised peptonised gelatin gave rise to other colouring matters than those named pyocyanin and pyoxanthin by Fordos. Certain aromatic substances are simultaneously formed. The cultivation was greenish-blue, and its odour that of limes. The following are the substances which were separated:—

1. An azure-blue pigment turned red by acids, and as sensitive as litmus. It dissolves in chloroform, from which it crystallises in the rhombic system. The absorption spectrum of the blue (alkaline) pigment shows two bands, (1) λ30—66, (2) λ150—ultra-violet. The absorption spectrum of the red (acid) pigment shows also two bands, (1) ultra-red—λ26, (2) λ40—ultra-violet. This substance is doubtless pyocyanin.

2. Pyocyanin being separated, the cultures remain coloured reddish-brown by reflected, emerald-green by transmitted light; when acidified the liquid loses its dichroism, which, however, returns when it is made alkaline once more. The colouring matter is a mixture of two pigments: one, soluble in alcohol, of a green colour by reflected, and blue by transmitted light; the other, insoluble in alcohol, is orange-red by reflected, greenish-blue by transmitted light. Neither of these corresponds with pyoxanthin, which is apparently not formed by the β bacillus.

3. The aromatic substances are not yet identified, a further communication on this part of the subject is promised; the methods adopted for their separation are briefly described. W. D. H.

Relation between the Assimilation and Transpiration produced by Chlorophyll. By H. JUMELLE (*Compt. rend. Soc. Biol.* [9], **1**, 9—10).—In sunlight, chlorophyll is stated to have two functions, that of assimilation of carbon from carbonic anhydride, and that of vaporising the water contained in the plant (transpiration). In order to investigate the relationship between these two phenomena, a certain number of plants were placed in air containing carbonic anhydride, and another number of similar plants in air free from carbonic anhydride; otherwise, the two sets of plants were under the same conditions. It was found that those in air free from carbonic anhydride, that is, those in which no assimilation was taking place, gave out more water than the other set. It thus appears that when assimilation is in abeyance, the greater part of the radiant energy absorbed from the light serves for the evaporation of water.
W. D. H.

Influence of Acids on the Evolution of Gases by Plants. By L. MANGIN (*Compt. rend.*, **109**, 716—719).—The researches of de Saussure, Mayer, and de Vries, have shown that Cactæ and Crassulaceæ, which contain a notable proportion of organic acids, have the power of evolving oxygen without absorbing carbonic anhydride when placed in sunlight, this change being accompanied by a reduction in the quantity of the organic acids.

The leaves of fusain, which contain practically no free acids, were injected with a dilute solution (2 to 3 per cent.) of some organic acid, and exposed to light. With malic, citric, and tartaric acids, oxygen was evolved, but acetic, formic, oxalic, and succinic acids gave negative results, probably because they killed the protoplasm. The volume of oxygen liberated varied with the nature of the acid, but, other conditions being the same, it was greatest with malic, less with citric, and least with tartaric acid. The volume of oxygen decreases with the concentration of the acid injected, because of the destructive action of the acid on the protoplasm.

The respiration of plants in the dark is also affected by the presence of free acid, the volume of oxygen absorbed, and the volume of carbonic anhydride liberated, being largely increased. Moreover, in normal leaves, the ratio CO_2/O is less than or at most equal to unity, whilst in presence of acids it is always greater than unity, and in some cases considerably greater.

The presence of certain organic acids in plants exerts a double influence. In the dark, it causes the evolution of a volume of carbonic anhydride greater than that of the oxygen absorbed, and, in light, the evolution of oxygen without a correlated absorption of carbonic anhydride. The cause of these disturbances is in the leaves themselves; the chlorophyll simply reduces, under the influence of light, the excess of carbonic anhydride which is exhaled by the tissues under the influence of the acids. C. H. B.

Formation of Calcium Oxalate in Plants. By KOHL (*Ann. Agronom.*, **15**, 418—420, from *Bot. Centr.*, **38**, 471).—The author's view is that asparagine and other amides are built up into albuminoïds with the aid of carbon and hydrogen derived from the carbohydrates. The oxygen liberated goes to form organic acids, especially oxalic, and this acid combines with the lime which is distributed through the tissues in combination with sugar and other soluble carbohydrates. The building up of the albuminoïds can only take place in the cells exposed to light; therefore the amides accumulate in any organ kept in the dark, and but little acid is found in these parts. In the parts exposed to light, acid is, on the contrary, abundant. When starch is stored up in roots, rhizomes, bulbs, seeds, &c., the lime which held the carbohydrate in solution is set free, and it is in these places that most calcium oxalate is found. In the Gramineæ much of the calcium oxalate is replaced by potassium oxalate.

J. M. H. M.

Calcium Oxalate in the Leaves of Alnus glutinosa, Symphoricarpus racemosa, and Cratægus oxyacantha. By C. WEHMER (*Ann. Agronom.*, **15**, 420—421, from *Bot. Zeit.*, 1889, 141, 165).—By comparing corresponding leaves in shoots of different age, the author concludes that there is no solution and migration of the calcium oxalate at first formed, as contended by Schimper, but that the deposits of oxalate increase at different rates in tissues of different age.

J. M. H. M.

Occurrence of Scatole in the Vegetable Kingdom. By W. R. DUNSTAN (*Pharm. J. Trans.* [3], **19**, 1010; and *Proc. Roy. Soc.*, **46**, 211).—From the wood of *Celtis reticulosa*, a tree which grows in Java, Ceylon, and Eastern India, and which when freshly cut has a very disgusting odour, the author has obtained a substance of the composition of scatole (3′-methylindole.) This corresponds in all its properties with synthetical scatole from propylidene phenylhydrazide. Indole is found with scatole in human fæces, but none was detected in the wood of *Celtis reticulosa*.

R. R.

Inulin in the Capitula of Composites. By L. DANIEL (*Compt. rend. Soc. Biol.* [9], **1**, 182—184).—Inulin has been found in the roots of a large number of composites, but has not been before noted in the capitules. It is, however, present in large quantities in the bracts, the receptacle, and even the seeds in course of development, especially in the Cynarocephala. It is always absent in parts exposed to light, and darkness appears to be favourable or perhaps essential for its elaboration.

The flowers were examined in different stages of development, and the conclusion drawn from these observations is that inulin is a reserve material, lasting, however, only a short time, and used up entirely in the development of the ovary and embryo.

W. D. H.

Analysis of White Soja Bean. By C. A. GOESSMANN (*Bied. Centr.*, 1889, 719).

	Seeds.				Whole plant on Aug. 30th, 1888.	
	Massachusetts.		New York.			
		Digestible matter.		Digestible matter.		Digestible matter.
	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
Moisture	17·38	—	5·85	—	6·12	—
Ash	5·22	—	5·57	—	6·47	—
Fibre	5·35	14·50	5·15	14·50	20·76	34·75
Fat	21·89	89·80	18·42	89·80	5·62	65·07
Albumin	33·36	90·00	35·98	90·00	15·87	57·45
Extractive	34·18	62·00	34·88	62·00	51·28	64·51

	H_2O.	CaO.	MgO.	K_2O.	Na_2O.	Fe_2O_3.
Seed	17·380	0·342	0·869	2·085	0·166	0·231
Whole plant	6·120	2·770	1·190	0·617	0·198	0·131

	P_2O_5.	N.	Insol. matter.
Seed	1·851	5·308	0·090
Whole plant	0·753	2·380	0·967

E. W. P.

Chemical Examination of Moorland and Peat Soils. By C. G. EGGERTZ and L. F. NILSON (*Bied. Centr.*, 1889, 664—668).—Various soils in Sweden were examined as to their volume-weight, percentage of organic matter and nitrogen, as well as of silicic acid, &c. The mineral constituents were dissolved out by a 2 per cent. solution of hydrochloric acid, and this strength of acid was found to be amply sufficient for the removal of all plant-food, and to render the soil sterile for barley; but to sterilise the fertile soils for oats, a 4 per cent. solution was requisite. These two solutions removed about equal quantities of silicic acid, which amounted to 0·1 per cent. of the dry soil. If the soil was exhausted with the acid, both directly and after ignition, then a very considerable difference in the quantities of sulphuric acid removed was noted, namely, 0·4 per cent. in the first case, and 0·96 in the second; also there was a great difference in the quantities of sulphates found, depending on the source of the soil, and the authors consider that, as the sulphates were not found in the hydrochloric extract, but only after ignition, the sulphur must be in many cases present as an organic compound. Only in 5 out of 32 cases did the sulphuric acid exceed 0·1 per cent., and it never amounted to 0·2 of the dried soil. The phosphoric acid estimations were of a similar kind, so that this element (phosphorus) must be considered as also being present in organic compounds, which are only rendered soluble by ignition; hence the advantage of burning a moorland soil without further addition of phosphatic manures.

In most cases the ignited soil yielded the most lime to dilute hydrochloric acid, the excess being 0·5—1·0 per cent. more than that found in the natural soil; but the opposite was found to be the case with the Gotland samples. A soil derived from Sphagnum, which contained only 0·22 per cent. of CaO, was completely sterile for oats, even after a heavy manuring with basic slag, potassium sulphate, and nitre, but 4,000 kilos. of chalk per hectare rendered it fertile. Concerning magnesium nothing remarkable was noticed; neither was much difference noticed in the case of potassium, except in those soils where potassium silicates were present in large quantities; these, being readily acted on by hot lime, naturally yielded after ignition a larger quantity of potassium to the acid.

The percentages of nitrogen varied from 1·38 to 4·57.

E. W. P.

Analytical Chemistry.

Filter Holder for Drying and Weighing. By C. REINHARDT (*Zeit. ang. Chem.*, 1889, 61).—This is a glass box, in shape like a funnel, with a short, wide neck, and having a light ground cover. The filter, whether full or empty, is dried in it whilst retaining its conical form, whereby not only is drying accelerated, but any subsequent treatment of the precipitate is much facilitated.

M. J. S.

Estimation of Sulphur in Burnt Pyrites. By G. LUNGE (*Zeit. ang. Chem.*, 1889, 239—240).—Of methods depending on the neutralisation of an alkali by the conversion of the sulphur into a sulphate in the dry way, that of Watson (Abstr., 1889, 306) is the only accurate, as well as the simplest and most expeditious one.

M. J. S.

Estimation of Nitrites. By W. R. DUNSTAN and T. S. DYMOND (*Pharm. J. Trans.* [3], **19**, 741—743).—The authors have devised an apparatus for titrating, in an air-free space, the iodine liberated by nitrites from an acid solution of potassium iodide. All sources of error are thus eliminated, and the process has distinct advantages over the gasometric methods, especially in the case of organic nitrites. A stout glass flask of about 100 c.c. capacity is fitted with an india-rubber stopper, through which passes a short glass tube connected with a small tube-funnel by means of a short piece of thick india-rubber tubing carrying a steel screw clamp. 5 c.c. of 10 per cent. potassium iodide solution, 5 c.c. of 10 per cent. sulphuric acid, and 40 c.c. of water are introduced, and the mixture boiled in the flask with the tubes open until all the air and iodine that may have been liberated have been expelled; when the steam is escaping freely from the funnel, the clip is closed tightly at the same moment that the source of heat is withdrawn. Then the flask is cooled. A known quantity of the nitrite solution, equivalent to about ·1 gram of nitrous acid, is placed in the funnel and cautiously drawn into the flask by unscrewing the clip, recently boiled water

being used for washing it down. The iodine liberated is estimated by a decinormal sodium thiosulphate solution, gradually introduced into the flask with due precautions for the exclusion of air. The colour of the dissolved iodine is a sufficient indicator, but starch may be used. Many test determinations of volatile organic nitrites are given, with the figures controlled by other methods. The results are very accordant, and speak well for the accuracy of the process.

R. R.

Estimation of Arsenic in Iron. By M. A. v. REIS (*Chem. Centr.*, 1889, ii, 379; from *Stahl. u. Eisen*, **9**, 720—723).—10 grams of pig iron is dissolved with 100 c.c. of water and 20 c.c. of concentrated sulphuric acid. The insoluble residue, consisting of those metals precipitable by hydrogen sulphide in acid solution, especially arsenic and copper, is collected, and dissolved with hydrochloric acid and potassium chlorate. The chlorine is expelled, the ferric chloride reduced by sodium hypophosphite, and the arsenic and copper precipitated by ammonium thiocarbamate, filtered, washed with dilute hydrochloric acid and water, then oxidised with concentrated nitric acid, filtered and the arsenic precipitated with magnesia mixture. The precipitate is washed into a platinum crucible with nitric acid, evaporated to dryness, and weighed after driving off the ammonium salts by ignition.

J. W. L.

Carbonic Oxide Detector. By RACINE (*Bull. Soc. Chim.* [3], **1**, 555—558).—To indicate the presence of deleterious quantities of carbonic oxide in dwelling rooms, an apparatus is described in which the fact, that guncotton dusted with platinum black fires in air containing 2·5 per 1,000 of carbonic oxide, is made use of to determine the closure of an electric circuit containing an alarum.

T. G. N.

Improvement in the Method of Estimating Carbonic Anhydride by Volume. By F. FUCHS (*Monatsh.*, **10**, 602—604).—The acid solution used to decompose the carbonate is previously saturated with and is kept in an atmosphere of carbonic anhydride, whereby the usual error due to the retention of the gas in the acid is avoided.

G. T. M.

Estimation of Silica and Analysis of Siliceous Material. By G. CRAIG (*Chem. News*, **60**, 227).—Taking into consideration the errors and difficulties attached to the estimation of silica by the method of fusion with alkaline carbonates, the author prefers to drive off the silica by means of hydrofluoric and sulphuric acids, and to estimate other substances in the residue. About 1·5 gram of finely-powdered substance is treated with sulphuric acid diluted with an equal volume of water, about 4 grams of pure hydrofluoric acid added, the whole mixed well by shaking gently, and heated over a small flame until almost dry; the operation is repeated, and the heating continued until sulphuric acid vapour is evolved in order to be sure that all the fluorides are decomposed. The residue is subsequently dissolved in hydrochloric acid and examined in the usual manner.

D. A. L.

Analysis of Sodium Sulphate. By ISBERT and VENATOR (*Zeit. ang. Chem.*, 1889, 66—67).—For many purposes a rapid and fairly

accurate estimation of the sodium sulphate in the commercial article is required. About 2 grams of the sample is dissolved in a little hot water, ammonia and ammonium carbonate are added, and the mixture is filtered; the precipitate is dissolved off the filter by hydrochloric acid, again precipitated as before, and then collected and thoroughly washed. A little sulphuric acid is added to the filtrates and washings, which are then evaporated in a platinum basin and ignited. From the weight of the residue is deducted the sodium sulphate corresponding to the sodium chloride in the original substance, as estimated by titration for chlorine. The remainder is the sodium sulphate in the substance taken. M. J. S.

Chromium and Barium in Foods. By L. DE KONINGH (*Arch. Pharm.* [3], **27**, 944; from *Ned. Tij. Pharm. Chem. Tox.*, 1889, 257).—At least 25 grams of the substance is burnt in a platinum dish, and the ash is weighed. To the ash is added four times its weight of potassium sodium carbonate and the same amount of potassium nitrate, and the whole is fused for 15 minutes. After boiling with water and filtering, the liquid is yellow if chromium is present; but the presence of manganese may produce a greenish colour, which is removed by boiling for a few minutes with a little alcohol. The liquid is then concentrated to 20 c.c., filtered into a test-tube, and compared with water to which potassium chromate solution is added until the two tints are of the same intensity. To prove that the colour is due to chromium, acidify with acetic acid and add lead acetate. If lead is present in the original substance, a yellow precipitate is obtained before the acetate is added. The portion of ash insoluble in water is dissolved in hydrochloric acid, and if lead is to be sought for, this is carefully neutralised before hydrogen sulphide is added. To detect barium carbonate, the strongly acid solution of the ash is treated with a large excess of calcium sulphate solution, by which the barium is quickly precipitated as sulphate free from lead, as the latter is readily soluble in the strong acid. J. T.

Magnesium as a Reagent. By H. N. WARREN (*Chem. News*, **60**, 187—188).—It is pointed out that magnesium, on account of its purity and activity, is an excellent reducing agent. In the dry way it reduces most metals, and even silica and boric anhydride when intensely heated in closed vessels with them. It does not reduce the alkalis and alkaline earths, but is attacked by molybdic anhydride with explosive violence. Being free from arsenic, it is well suited for use in Marsh's test, and as it contains neither iron, phosphorus, nor sulphur, scarcely reacts with potassium ferricyanide, and is more active than zinc, it may be used with advantage for reducing ferric to ferrous salts. If a solution of zinc acetate is boiled with magnesium, the whole of the zinc is precipitated, even though the solution also contains metals of the fourth group.

Iron may be separated from chromium in the following manner: the acid solution of iron and chromium is precipitated with sodium carbonate, the precipitate dissolved in acetic acid and magnesium added. The reducing action is at first violent and then ceases, but

on applying heat, the colour of the solution changes from green through pink, red, violet back to green, the iron in the meantime being precipitated on the magnesium. D. A. L.

Volumetric Estimation of Zinc. By A. VOIGT (*Zeit. ang. Chem.*, 1889, 307—308).—The solution of the substance in hydrochloric acid is oxidised with nitric acid and diluted to about 100 c.c. Sufficient potassium tartrate to keep the iron in solution is added, and then ammonia to feeble alkalinity, and the liquid is further diluted to about 250 c.c. Standard solution of potassium ferrocyanide is then run in, until a drop of the mixture brought in contact with strong acetic acid develops a permanent blue. The ferrocyanide is of suitable strength if 1 c.c. is equal to 0·01 gram of zinc. About 46 grams of the salt is dissolved to a litre, and the solution is standardised against one of zinc made by dissolving 12·461 grams of zinc oxide in hydrochloric acid and diluting to a litre; 10 c.c. of this solution is mixed with 5 grams of potassium tartrate, a few drops of ferric chloride, ammonia, and water to 250 c.c., and should require 10 c.c. of the ferrocyanide. An essential condition is that the excess of ammonia should be as small as possible. Incorrect results are obtained when much manganese is present; lead is not injurious. The process is more rapid than Schaffner's. M. J. S.

Standardisation of Permanganate. By R. JAHODA (*Zeit. ang. Chem.*, 1889, 87).—In dissolving iron wire for the above purpose, the flask is fitted with a cork and a bent tube which dips into a beaker containing solution of sodium hydrogen carbonate. Any of this solution drawn in during the cooling of the iron solution produces an evolution of carbonic anhydride in the flask. M. J. S.

Incineration of Vegetable Matter. By G. LECHARTIER (*Compt. rend.*, **109**, 727—731).—When vegetable matter is incinerated with free exposure to air or in a current of oxygen, there is always volatilisation of a portion of the sulphur, which may be absorbed by conducting the operation in a retort and passing the products of decomposition through a tube containing sodium carbonate.

Phosphorus, however, is not volatilised, if the matter is first carefully carbonised and then incinerated in presence of air or oxygen.

Incineration is best conducted in a platinum dish with a glass funnel supported a short distance above it. The temperature is raised very gradually, and when thoroughly carbonised the residue is extracted with warm water, washed, and the insoluble portion moistened thoroughly with milk of lime, dried, and heated until all carbonaceous matter is burnt away. The phosphoric acid in the aqueous solution and the final residue is estimated in the usual way.

C. H. B.

Water Analysis. (*Chem. News*, **60**, 203—204.) *Report of the Committee appointed by the British Association to confer with the Committee of the American Association with a view of forming a uniform system of recording results of Water Analysis*; B. A. Meeting, 1889.—The committee recommend a system of statement for a complete analysis of which the following is an epitome. Results to be expressed in parts

per 100,000. In a potable water, the numbers to be given in the following order:—Total solid matters, (*a*) in suspension, (*b*) in solution; organic carbon; organic nitrogen; oxygen consumed, as indicated by decoloration of permanganate; ammonia expelled on boiling with sodium carbonate; ammonia expelled on boiling with alkaline permanganate; nitrogen as nitrates and nitrites; chlorine; hardness—temporary, permanent, total; in a mineral water—carbonate of lime; carbonate of magnesia; carbonate of soda (calculated from residual alkalinity after boiling and filtering off precipitated $CaCO_3$ and $MgCO_3$); total of each of the following elements—calcium, magnesium, potassium, sodinm, iron (ferrous), iron (ferric), and each of the following radicles—sulphuric (SO_4), nitric (NO_3), nitrous (NO_2), phosphoric (PO_4), silicic (SiO_3); then each of the elements—chlorine, bromine, and iodine, and of sulphur as sulphide. *Dissolved gases;* c.c. at 0° C. and 760 mm. in 1 litre of water. Carbonic anhydride (CO_2); oxygen; nitrogen; sulphuretted hydrogen.

They consider that this uniform method should be adopted in all cases where communications come before learned bodies and whenever possible in professional practice; that the decimal numerical notation is to be preferred; that the different scales for potable and mineral waters suggested by the American Committee are undesirable; that all results obtained by calculation should be sharply distinguished from those obtained by direct determination; that a statement of mineral constituents combined as *salts* is not to be approved of unless the analytical data upon which it is based are clearly stated; that the American Committee's suggestion of recording the proportion of each element of binary compounds, and recording all the oxygen in oxy-compounds in combination with the negative element, as indicated above, is the most convenient for all purposes of calculation, although the want of a name for these negative groups and the custom of quoting metallic elements as bases are objections to this system; finally, that volumes of dissolved gases may be given as above or in volumes of gas per 100 volumes of water. D. A. L.

Estimation of Carbonic Acid in Potable Waters containing Magnesia. By H. TRILLICH (*Zeit. ang. Chem.*, 1889, 337).—100 c.c. of the water is mixed in a stoppered cylinder with 5 c.c. of barium chloride solution (1 : 10) and 45 c.c. of titrated baryta-water (7 grams of barium hydroxide and 0·2 gram of chloride per litre) and allowed to subside for 12 hours. Two quantities of 50 c.c. each are then removed without disturbing the sediment and are titrated with hydrochloric acid, of which 1 c.c. equals 1 mg. of carbonic anhydride (using phenolphthaleïn). The magnesia is determined gravimetrically. Putting a for the number of c.c. of acid required by 45 c.c. of the baryta, b for the acid required by 50 c.c. of the clarified mixture, and m for the number of milligrams of magnesia in 100 c.c., then $10(a - 3b - 1{\cdot}1m)$ gives the number of milligrams of free and loosely-combined carbonic anhydride per litre. The remaining 50 c.c. in the settling vessel with the precipitate is titrated with the same acid (using cochineal). If d is the number of c.c. used, $10(d - b - 1{\cdot}1m)$ is the total carbonic anhydride in milligrams per litre. M. J. S.

Standard Solution for Clark's Soap-test. By F. E. NELSON (*Chem. News*, **60**, 132).—The author suggests the following mode of preparing a standard soap solution of constant composition :—A gram of pure palmitic acid is dissolved in a little pure spirit, neutralised with 4 c.c. of normal soda solution and diluted to 200 c.c. with so much aqueous spirit as to retain 35 per cent. of alcohol in the standard solution. Fatty acids separated from ordinary tallow may be used instead of palmitic acid.

D. A. L.

Detection of Mercuric Cyanide in Toxicological Investigations. By D. VITALI (*Chem. Centr.*, 1889, ii, 391—392; from *L'Orosi*, **12**, 181—196).—The author recommends the following modification of Selmi's method for the detection of mercuric cyanide in toxicological investigations.

The substance is acidified with tartaric acid, neutralised again with precipitated calcium carbonate, a slight excess of aqueous hydrogen sulphide solution added, the flask closed and allowed to remain at rest for 24 hours in the cold, then a further quantity of hydrogen sulphide water is added and a current of hydrogen passed through the liquid. The gases are passed first through a solution of bismuth nitrate in dilute nitric acid to absorb the hydrogen sulphide, and secondly through aqueous potash for absorption of hydrogen cyanide; in the latter solution, the usual tests for hydrogen cyanide may be made.

J. W. L.

Reaction of Sodium Nitroprusside with Alkaline and Alkaline Earthy Hydroxides. By H. BRUNNER (*Chem. News*, **60**, 168).—Sodium nitroprusside produces an intensely yellow coloration with sodium, potassium, barium, or calcium hydroxide, but does not react with the soluble carbonates or hydrogen carbonates.

By adding aqueous sodium nitroprusside to sodium hydroxide until an orange-colour appears, shaking with alcohol and allowing to settle, a deep-yellow oil separates, which ultimately solidifies to orange-coloured crystals. An aqueous solution of this salt gives coloured precipitates with metallic salts; moreover, with acids it gives a green colour, becoming violet on exposure to the air, finally giving a green precipitate.

D. A. L.

Estimation of Glycerol by Oxidation with Permanganate in Acid Solution. By H. GRÜNWALD (*Zeit. ang. Chem.*, 1889, 34—35).—Planchon's method (Abstr., 1888, 1345) affords very serviceable results; in 12 determinations, the mean error of a single result was 1·81 per cent. Potash in Liebig's bulbs is, however, more suitable than soda-lime for absorbing the carbonic anhydride.

M. J. S.

Copper Solution for the Estimation of Glucose. By E. SOLDAINI (*Chem. Centr.*, 1889, ii, 389—390; from *L'Orosi*, **12**, 196—198).—The author recommends a more dilute solution of cupric sulphate in potassium hydrogen carbonate than that generally described under the name of "Soldaini's solution" (compare Abstr.,

1889, 313). 3·464 grams of cupric sulphate (5 aq.) and 297 grams of potassium hydrogen carbonate are dissolved in 1 litre.

This solution will detect 0·0005 gram of glucose in 10 c.c. of water by boiling with the reagent for 10 minutes. For quantitative purposes it is applied as when using Fehling's reagent, approximate tests being first made, and finally the quantity thus found added all at once to the copper solution and boiled for five minutes, when an excess of neither copper nor sugar should be present.

J. W. L.

Iodine Absorption of Essential Oils. By R. H. DAVIES (*Pharm. J. Trans.* [3], **19**, 821—824).—This paper records the results of the application of Hübl's reagent to determine the "iodine absorption" of essential oils. A weighed quantity of the oil was allowed to remain all night with an excess of the iodine solution. The differences were greater than those found with fixed oils, as they ranged from 0 to nearly 400 per cent. A table of the results obtained with 64 essential oils and their derivatives shows the percentages obtained. Oil of almonds is *nil*, menthol 0·12, camphor 0·46 per cent. English and Japanese oil of peppermint 43·5 to 57·7 per cent.; but American, 121·8 to 132·2. Thymol and anethoïl 171·5 to 182·9 per cent.

R. R.

Testing Oil of Peppermint for Adulterants. By H. W. SNOW (*Pharm. J. Trans.* [3], **19**, 1056—1058).—The author gives the results of his trials of some tests which have been proposed for detecting the presence of certain adulterants in oil of peppermint. When 5 per cent. or more of alcohol has been added, the oil will be coloured distinctly red on agitating it for a few seconds with a little magenta, which is insoluble in the perfectly pure oil. Oil of camphor may be detected by agitating two drops of the sample with a little nitric acid (sp. gr. 1·42), when a reddish-brown colour may appear, even in the absence of oil of camphor, but this fades in two or three hours, while the distinct red colour due to the presence of this adulterant persists for two days. For detecting turpentine, the optical test is not conclusive, as French oil of turpentine has itself left-handed rotation. The non-solubility of turpentine in 80 per cent. alcohol fails to detect even 50 per cent. of it when mixed with oil of peppermint. Fractional distillation is useful, and when followed by determinations of the iodine absorption, trustworthy indications may be obtained in certain cases. Gold chloride in chloroform solution, boiled with a few drops of an essential oil, gives characteristic reactions. Oil of turpentine reduces the solution quickly with little or no colour; oil of camphor acts slowly with only a faint-blue colour; oil of copaiba gives a fine blue solution which gradually loses its colour; oil of peppermint quickly gives a brown, changing into violet-red. These reactions can, however, seldom be used with confidence, except under special circumstances. R. R.

Reactions of Essential Oils. By R. WILLIAMS (*Chem. News*, **60**, 175—176).—The author has examined a great number of essential oils with regard to their potash and iodine absorption, noting also their boiling points and specific gravities; a table of results is given.

In his opinion concordant results have been obtained with oils of bergamot, caraway, cassia, cedar-wood, cinnamon, citron, citronelle, cloves, lemon, mace, nutmeg, orange, thyme, and verbena, and it is suggested that by examining these oils in this manner adulterations may be detected with certainty. Oils of aniseed, cajeput, eucalyptus, juniper, lavender (various), spike, lemon grass, pennyroyal, peppermint (various), rosemary, rue, sage, and sassafras, did not yield concordant results, for which various causes are assigned, such as adulteration, difference in age, and change in composition. Oil of spike has a lower boiling point and a lower potash absorption than the more expensive oil of lavender. Oil of cinnamon has a lower gravity, boiling point, and potash absorption, but a much higher iodine absorption than the cheaper oil of cassia. At least two, and in some cases more samples of each oil have been examined. D. A. L.

Reactions of Essential Oils. By R. A. CRIPPS (*Chem. News*, **60**, 236).—In reference to the iodine absorption of essential oils, attention is called to the importance of time and temperature in these reactions; the latter has already been recognised by both R. H. Davies and H. W. Snow (preceding page), but disregarded by R. Williams (preceding abstract). The author now compares the results obtained by Barenthin, Davies, Snow, and Williams; there are discrepancies which are probably due to want of uniformity as regards the two factors mentioned above. H. W. Snow, in a letter (*Chem. News*, **60**, 245), points out that he found the iodine absorption extremely useful in connection with the examination of oil of peppermint for adulteration with oil of turpentine; he also gives references his own contributions and to the work of others on the subject.

D. A. L.

Tests for Fixed Oils. By F. X. MŒRK (*Pharm. J. Trans.* [3], **19**, 785).—A reaction proposed by Hirschsohn (Abstr., 1889, 658) for the detection of cotton-seed in other fixed oils was to mix 5 c.c. of the oil with 10 drops of a chloroform solution of gold chloride (1 gram in 200 c.c.), and to heat to 100°. The red coloration produced in from three to five minutes is found by the author not to be characteristic of cotton-seed oil, for he has obtained the like result with the oils of arachis, ben, poppy, sesame, walnut-kernel, &c. The paper contains extended lists of the gold chloride, and also of the silver nitrate reactions with these and many other kinds of fixed oils—pure, doubtful, and commercial. R. R.

Estimation of Neutral Fats. By M. GRÖGER (*Zeit. ang. Chem.*, 1889, 61—62).—In the saponification of a neutral fat by alcoholic potash, it does not suffice to boil for half an hour with a bare excess of the alkali, but it is necessary that the excess should not be less than a certain amount. For 5 grams of fat, the residual alkali ought to consume at least 5 c.c. of semi-normal acid, otherwise saponification is very liable to be incomplete. This may account for many of the recorded variations in the saponification equivalents of fats.

M. J. S.

General and Physical Chemistry.

Phosphorescence of Copper, Bismuth, and Manganese in the Sulphides of the Alkaline Earth Metals. By V. KLATT and P. LENARD (*Ann. Phys. Chem.* [2], **38**, 90—107).—The difference in the colour of the light emitted by the phosphorescent sulphides of metals of the alkaline earths when prepared by different methods, has hitherto been attributed to a difference in physical structure. The authors find, however, that the difference is really a chemical one, the above sulphides being, when pure, practically without phosphorescence, and only exhibiting this phenomenon when containing traces of the sulphides of copper, bismuth, manganese, or some fourth metal not yet identified, the colour of the phosphorescence varying with the nature and proportions of the active sulphides present. The presence or absence of any of the above metals can readily be ascertained, as each gives rise to a characteristic band in the spectrum of the phosphorescent material, the position of which is always the same. The intensity of the phosphorescence increases with the amount of active sulphide present, up to a certain point, but, when a maximum is reached, any further addition causes a decrease in the intensity, and ultimately destroys the phosphorescence. The quantities of active sulphide necessary to produce the above maximum are very small. In order to produce the brightest phosphorescence, a third substance should be present in addition to the above. This consists of some colourless salt which is fusible at the temperature required for the preparation of the phosphorescent sulphides. It will therefore form a thin layer on the surface of the sulphide, to which the active metal imparts a faint coloration, essential to the production of phosphorescence. H. C.

Refractive Indices of Gases. By T. P. DALE (*Phil. Mag.* [5], **28**, 268—271).—The author has observed certain empirical relations between the specific refractive energies of gaseous elements and between the logarithms of these values. Thus the logarithms of the specific refractive energies of nitrogen, chlorine, and phosphorus are identical, as also are those of sulphur and oxygen. The logarithms of the first three are double, and those of sulphur and oxygen $1\frac{1}{2}$ times that of hydrogen. The logarithm of the specific refractive energy of mercury is 8 times, and that of arsenic 9 times this quantity. Again, the specific refractive energy of oxygen is nearly double that of hydrogen, that of mercury 4 times, of arsenic 8 times, of sulphur 12 times that of hydrogen. Amongst compounds, the log. specific refractive energy of nitrous oxide is half that of carbonic oxide, whilst that of cyanogen is 6 times that of hydrogen. The author is engaged on the relations between the molecular weight and refraction of gases. H. K. T.

Refractive Indices of Salt Solutions. By B. WALTER (*Ann. Phys. Chem.* [2], **38**, 107—118).—The author finds from his own observations and those of others that the refraction of salt solutions is subject to laws similar to those for the reduction of the freezing point. Thus the index of refraction of a salt solution is proportional to the amount of salt dissolved. Solutions containing equal numbers of molecules of salts of monad metals with monobasic acids have the same refractive index, other similar solutions of salts of monad metals with bibasic acids have a refractive index which is practically double the above, and those of salts of diad metals have a refractive index which is three times that of the first. These laws hold even for concentrated solutions, and there is nothing to indicate the formation of hydrates in any of the solutions examined. The behaviour of cupric chloride in solutions containing more than 11 per cent. of the salt is abnormal, as the refraction of such solutions is greater than it should be according to the above rules, and points to the existence of molecules of greater complexity in the more concentrated solutions. This is supported by the well-known difference in colour of the concentrated and dilute solutions. A similar change is exhibited by potassium ferricyanide solutions at a concentration of 4 per cent. Fluoresceïn solutions were also examined up to a concentration of 40 per cent., in order to ascertain if any other molecular change, than that already recorded (Abstr., 1889, 553) at 2 per cent., could be detected, but with negative result. H. C.

A Standard Clark Cell. By H. S. CARHART (*Phil. Mag.* [5], **28**, 420—423).—The author finds that local action takes place in Clark cells owing to contact between the zinc and the mercurous sulphate, the temperature coefficient being thereby altered. He has constructed a cell in which contact is prevented. The new cell has a temperature coefficient less than that of Lord Rayleigh's cell; moreover its temperature coefficient decreases with rise of temperature. The polarisation is negligible for external resistances greater than 10,000 ohms. H. K. T.

Electromotive Forces of Cells containing Mixed Salt Solutions. By G. F. R. BLOCHMANN (*Ann. Phys. Chem.* [2], **37**, 564—575). —The E.M.F. of the standard Clark cell, Hg | Hg_2SO_4 | $ZnSO_4$ | Zn, decreases with rise of temperature, whereas that of the Helmholtz cell, Hg | Hg_2Cl_2 | $ZnCl_2$ | Zn, increases. By mixing the chlorides and sulphates of the metals, the author hoped to obtain a cell that would remain unaffected by change of temperature, but a cell containing mixtures in the proportions calculated to effect this result was found to differ but slightly from the chloride cell in its behaviour with respect to temperature. The author was therefore led to further investigate the E.M.F. of cells containing mixed salt solutions. Copper and zinc were selected as electrodes, the copper being immersed in a solution of two copper salts contained in a porous pot, surrounded by a solution of two similar zinc salts in which the zinc electrode is placed. The salts used were the sulphates,

chlorides, and nitrates of the metals, in solutions containing 1 mol. of salt to 50 mols. of water, and the acetates dissolved in the proportion 1 to 250. The results obtained with the various mixtures are tabulated and given in curve form. Cells containing the sulphates and chlorides, sulphates and acetates, and the chlorides and acetates give electromotive forces which practically correspond with the mean of those of cells containing the unmixed solutions, taken in the ratio in which the salts are mixed. The E.M.F. of the other cells containing the nitrates is usually below that thus calculated; but in the case of mixtures of nitrates and acetates containing a large excess of nitrate, the E.M.F. is greater than the theoretical. The exceptions in these latter cases are probably due to the fact that the salts have some chemical action one on another, which may in some way be connected with the partial dissociation which such salts undergo in aqueous solution. **H. C.**

Specific Inductive Capacity of Water. By E. COHN (*Ann. Phys. Chem.* [2], **38**, 42—52).—The author confirms the former result obtained by himself and Arons (Abstr., 1888, 394) for the sp. ind. cap. of water, in this case using the method originally employed for liquids of low conductivity (*Ann. Phys. Chem.* [2], **28**, 454). **H. C.**

Variations in the Electrical Resistance of Nitrogen Peroxide with a Rise of Temperature. By J. J. BOGUSKI (*Compt. rend.*, **109**, 804—806).—Nitrogen peroxide has a very high resistance, but the conductivity becomes recognisable and measurable in presence of 0·01 to 0·1 per cent. of water. No absolute measurements were made, but the relative resistances at different temperatures were determined. Concordant results were obtained with different methods of measurement.

The resistance increases as the temperature rises, and above 70° the peroxide is an almost perfect insulator. Abrupt variations are observed between 0° and 17°. Although a rise of temperature is accompanied by a definite and static increase in resistance, this is preceded by a temporary dynamic reduction of resistance, which is greater the more suddenly the compound is heated. This temporary variation is so considerable that it can readily be recognised if a lamp, or the body of the observer, is moved towards the tube containing the peroxide, provided that the latter is at a lower temperature.

The phenomena are doubtless connected with the dissociation of the peroxide. Neither NO_2 nor N_2O_4 is decomposed by an electric current, and hence they are insulators when separate and when mixed. The dissociation produced by heat sets up atomic movements favourable to the conduction of electricity by convection, and hence the resistance diminishes. These atomic motions soon cease, because the atoms form new molecules. A new condition of equilibrium is established, and the resistance acquires its normal static value.

If the peroxide is cooled suddenly, the variation of the resistance is always in the same direction, and no oscillations are observed similar to those produced by heating. C. H. B.

Change in Freshly-prepared Solutions. By E. PFEIFFER (*Ann. Phys. Chem.* [2], **37**, 539—563).—The author has noticed in former experiments (Abstr., 1886, 115) that if a solution is allowed to remain for some length of time, the electrical conductivity often undergoes a temporary decrease, and that this continues until a minimum is reached, from which it again increases. The author now finds that this occurs with water which is left freely exposed in the ordinary way, but not with water which has been kept out of contact with the atmosphere or only exposed to purified air. The phenomenon is, therefore, in some manner due to the impurities of the atmosphere. The change becomes more pronounced if the solution is acidified slightly, and the more so the greater the amount of acid added, whereas basic substances produce just the opposite effect, and neutral salts are practically without action. As carbonic acid is among the acids which have the above effect, and ammonium carbonate is a much better conductor than free ammonia in aqueous solution, the change is in all probability not due to the ammonia in the atmosphere. It might, however, be due to organic impurities. H. C.

Electrical Conductivity as a Means of Investigating the Interaction of Acids of Complex Function. By D. BERTHELOT (*Compt. rend.*, **109**, 801—804).—The author has utilised determinations of electrical conductivity in order to determine the conditions of equilibrium between dilute saline solutions and aspartic acid, which combines the functions of a base and an acid. Solutions were employed containing a gram-equivalent of the acid or salt in 100 litres. With this degree of dilution, variations in molecular conductivity with variations in the concentration of the solution, are sufficiently small to be negligible.

The conductivity of a mixture of aspartic acid and sodium chloride indicates decomposition to the extent of 4 per cent., and precisely the same final system is obtained by mixing sodium aspartate with hydrochloric acid, the decomposition in this case amounting to 96 per cent. In the first case, the addition of a second or third molecule of aspartic acid or sodium chloride has no appreciable effect. In the second case, if two molecular proportions of sodium aspartate are mixed with one molecular proportion of hydrochloric acid, the observed conductivity is lower than that calculated on the assumption of complete decomposition, a result due to interaction between sodium aspartate and aspartic acid, and, in a much lower degree, between sodium aspartate and sodium chloride. A third molecular proportion of sodium aspartate exerts a slight but distinct additional influence in the same direction. C. H. B.

Electrical Conductivities and Multiple Affinities of Aspartic Acid. By D. BERTHELOT (*Compt. rend.*, **109**, 864—867).—In this paper the author investigates the basic functions of aspartic acid, the methods of measurement being identical with those used in the investigation of its acid functions (preceding abstract). The addition of an equivalent proportion of hydrochloric acid to aspartic acid produces a very marked diminution in the electrical resistance; this

indicates a reduction in the number of molecules, owing to combination between the two acids. A second equivalent of hydrochloric acid produces about one-fifth of the reduction produced by the first. A second equivalent of aspartic acid produces half the reduction of the first, and a third equivalent produces one-fourth of the original reduction.

The addition of aspartic acid to sodium aspartate increases the resistance, owing to the formation of a double salt, but the effect of successive quantities of aspartic acid gradually diminishes.

The addition of an equivalent of sodium hydroxide to sodium aspartate is accompanied by a very considerable increase in resistance; a second equivalent of alkali produces an effect only one-third as great, and this is true also of a third equivalent. A second equivalent of aspartate has a comparatively small effect, and a third or fourth equivalent has still less.

Sodium chloride and sodium aspartate, in equivalent proportions, form a small quantity of a double salt, but a further quantity of either salt has but little influence on the result. C. H. B.

Correction of Thermometric Readings for the Column Outside the Heating Medium. By E. Rimbach (*Ber.*, **22**, 3072—3075).—The author has made a large number of observations with various thermometers of Jena glass, in order to determine the correction which must be made in the observed reading when only part of the mercurial column is surrounded by the heating vapour. The very numerous observations, which are given in tabular form, show that Kopp's (*Annalen*, **94**), Holtzmann's (*Handwörterbuch der Chemie*, **7**, 368), and Thorpe's (Trans., 1880, 160) corrections give results which are too low with long threads, and too high with short ones; the error in the case of long threads may be more than one degree when Holtzmann's or Thorpe's correction is employed.

Mousson's constant (*Ann. Phys. Chem.*, **133**, 311) has not a constant value in the case of high-registering thermometers, and the error in determining this constant, as recommended by Mousson, may amount to 0·7 degree. Wüllner's value for $\sqrt{h/\kappa}$ is also variable.

F. S. K.

Experimental Determination of the Ratio of the Specific Heats in Superheated Steam. By R. Cohen (*Ann. Phys. Chem.* [2], **37**, 628—633).—From the velocity of sound in superheated steam, the ratio of the specific heats k was determined by a method similar to that used by Strecker in the case of chlorine, bromine, and iodine. The mean value for k thus found was 1·287, the temperature varying from 144° to 300°; between these temperatures no change in the constancy of k being observed. From the equation of Clausius for the relation between volume, pressure, and temperature in any vapour, the values of k for other temperatures can be calculated, and such a calculation gives a value of 1·333 at 95°, agreeing with that found by Jaeger (Abstr., 1889, 460) and other observers. The author does not, however, place reliance in such a calculation, as the

Clausius equation is no longer truly applicable to superheated vapours. H. C.

Animal Heat and the Heat of Formation and Combustion of Urea. By BERTHELOT and P. PETIT (*Compt. rend.*, **109**, 759—764). —The combustion of urea was readily effected in the calorimetric bomb, the heat of combustion for 1 gram being 2530·1 Cals., or $CO(NH_2)_2 + O_3 = CO_2$ gas + N_2 gas + $2H_2O$ liquid, develops +151·8 Cals. at constant volume, or +151·5 Cals. at constant pressure. The formation of solid urea from carbon (diamond) and its gaseous constituents liberates +80·8 Cals. The heat of dissolution at about 11° is —3·58 Cals., and hence the heat of formation in solution in water (or urine) is +77·2 Cals., and its heat of combustion +160·9 Cals.

The formation of solid urea and liquid water from carbonic anhydride and ammonia would liberate +31·1 Cals., and the formation of the dissolved compound from dissolved carbonic anhydride and dissolved ammonia, would liberate +4·3 Cals. The formation of urea from ammonium carbonate (both in solution) would absorb —6·4 to —8·0 Cals., and hence this change does not take place directly, but the reverse change liberates +6·4 to +8·0 Cals., and hence readily occurs under favourable conditions. The conversion of ammonium cyanate into urea liberates about +7·1 Cals. The complete combustion of urea liberates 11·8 Cals. less than the combustion of its constituents, if they were in the free state, but this complete oxidation only takes place under exceptional conditions. It seems, in fact, that nitrogen in the form of amido-compounds oxidises with much greater difficulty than carbon and hydrogen, is capable of being converted into ammonia, and when introduced into the organism in the form of food, is excreted again with a very small loss of its energy. C. H. B.

Specific Gravity Apparatus. By BAILHACHE and COMMELIN (*Bull. Soc. Chim.* [3], **2**, 196—198).—This apparatus is intended for the determination of the volume of vegetable products, such as fruits, roots, &c. By means of an iron plunger, the substance is kept immersed under the surface of mercury, contained in a vessel communicating by a U-tube with a cylinder containing the same metal above the surface of which is placed coloured alcohol; any displacement of mercury in the former vessel causes the alcohol to enter an upright narrow, calibrated tube, and thus the volume of the mercury displaced, and consequently that of the substance, is determinable.

T. G. N.

Dissociation of Salts containing Water, and the Constitution of the Combined Water. By W. MÜLLER-ERZBACH (*Ber.*, **22**, 3181—3182).—The author gives a list of salts containing water of crystallisation; those molecules of water which show a greater tension being placed in the table to the right and separated by a + sign.

$Na_2HPO_4 + 2H_2O + 5H_2O + 5H_2O$,	$MnCl_2 + H_2O + H_2O$,
$Na_2CO_3 + H_2O + 9H_2O$,	$BaCl_2 + H_2O + H_2O$,
$Na_2B_4O_7 + 5H_2O + 5H_2O$,	$NaS_2O_3 + 2H_2O + 3H_2O$,
$Na_2SO_4 + 10H_2O$,	$PbC_4H_6O_4 + 3H_2O$,
$MgSO_4 + H_2O + 5H_2O + H_2O$,	$NaC_2H_3O_2 + 3H_2O$,
$NiSO_4 + H_2O + 5H_2O + H_2O$,	$CaN_2O_6 + 2H_2O + H_2O$ (?),
$CoSO_4 + H_2O + 5H_2O + H_2O$,	$CaN_2O_6 + 4H_2O$,
$FeSO_4 + H_2O + 3H_2O + 3H_2O$,	$CaN_2O_6 + 2H_2O + H_2O$,
$ZnSO_4 + H_2O + H_2O + 5H_2O$,	$ZnN_2O_6 + 3H_2O + H_2O + H_2O$,
$CuSO_4 + H_2O + H_2O + H_2O + 2H_2O$,	$AlK(SO_4)_2 + 3H_2O + 9H_2O$,
$MnSO_4 + H_2O + H_2O + 3H_2O$,	$Al(NH_4)(SO_4)_2 + 3H_2O + 9H_2O$,
$CaCl_2 + H_2O + H_2O + 2H_2O + 2H_2O$,	$AlNa(SO_4)_2 + 6H_2O + 6H_2O$,
$MgCl_2 + 4H_2O + 2H_2O$,*	$CrK(SO_4)_2 + 6H_2O + 6H_2O$,
$CoCl_2 + 2H_2O + 4H_2O$,	$BaH_2O_2 + H_2O + H_2O + 5H_2O + H_2O$,
$NaBr + 4H_2O$,	$SrH_2O_2 + H_2O + 6H_2O + H_2O$.

* Only decomposed to $MgCl_2 + 4H_2O$.

In the case of copper sulphate, the second and third molecules of water cannot be separated in this way at temperatures above 40°.

F. S. K.

Osmosis with Living and Dead Membranes. By E. W. Reid (*Brit. Med. J.*, 1890, i, 165—167).—See this vol., p. 277.

Specific Volume of Aqueous Vapour. By C. Dieterici (*Ann. Phys. Chem.* [2], **38**, 1—26).—This paper deals with the determination of the specific volume of water vapour saturated at 0°. The author has previously determined the heat of vaporisation of water at 0°, which is 596·8 cal. per gram, and now employs this quantity to determine the weight of water converted into vapour at 0°, and occupying a certain known volume. With the ice calorimeter, as small a quantity of heat as 0·03 cal. is still measurable, and therefore, although at 0° a volume of 5 litres would only contain 25 milligrams of saturated water vapour, this weight can be determined by the above method to within 0·2 per cent., the error of a direct weighing being about 4 per cent. The only other serious source of error is in the condensation which takes place on the surface of the glass, which is particularly marked if the vessel which is to contain the vapour is exhausted as far as possible. This error is very materially reduced by selecting a glass of as insoluble a variety as possible, boiling well with water to remove alkali, and allowing a small quantity of air to remain in the exhausted vessel.

The results show that water vapour saturated at 0° obeys Gay-Lussac's law for perfect gases down to the saturation point. The density of the vapour is 0·0048856 milligram / c.c., and therefore the specific volume at 0 °is 204·68 c.c. / milligram. Since water vapour saturated at 0° behaves like a perfect gas, the density corresponds with that which might be deduced from Avogadro's law. The pressure which it exercises may, therefore, be calculated, and is found to be 4·619 mm. The above numbers are correct to within 0·5 per cent.

H. C.

Molecular Constitution of Isomeric Solutions. By G. Gore (*Phil. Mag.* [5], **28**, 289—303; compare Abstr., 1889, 90, 200, 201, 665, and 810).—The author examines by means of the voltaic balance the

distribution of base when equivalent quantities of sulphuric and nitric acids and sodium hydroxide are brought together. According to the researches of J. Thomsen, the final result is the same whether sodium sulphate is added to nitric acid or sodium nitrate to sulphuric acid, or sodium hydroxide to mixed nitric and sulphuric acids. The author has examined the voltaic energies of two mixtures, one A, consisting of $Na_2SO_4 + 2HNO_3$, the other B, consisting of $2NaNO_3 + H_2SO_4$. The general results of the investigation are that the solution B proceeds at once to the final distribution of soda between the acids ($\frac{2}{3}$rds of the soda to the nitric acid and $\frac{1}{3}$rd to the sulphuric acid), whilst the solution A, if very dilute or mixed at a low temperature, shows a voltaic energy approaching that of its separate constituents, and that it is only after a very considerable lapse of time or after a short ebullition that it approximates to the value found for B. Further, it has been found that a number of molecular compounds of the acids and salts with one another are formed when A is first prepared. Hence the order of mixing has a considerable influence on the voltaic energy of the freshly prepared solution. In the solution B, the evolved nitric acid probably unites with an equivalent quantity of the free sulphuric acid. Loss of voltaic energy does not necessarily involve loss of thermal energy, since the solution A absorbs heat when mixed, whilst B develops heat (Thomsen), both changes being accompanied by loss of voltaic energy. H. K. T.

Inorganic Chemistry.

Density of Fluorine. By H. MOISSAN (*Compt. rend.*, **109**, 861—864).—Fluorine was obtained by electrolysis, as before, but a larger apparatus was used, and in order to purify the gas completely from hydrogen fluoride, it was passed through a platinum worm cooled to $-50°$ by means of methyl chloride, and then through a platinum tube containing anhydrous sodium fluoride, which combines with hydrogen fluoride with great energy. The sodium salt is far preferable to the potassium salt, because it is not hygroscopic.

The pure fluorine was collected in platinum flasks of about 100 c.c. capacity, which had been previously filled with nitrogen. After being weighed, the fluorine was brought in contact with water, and the evolved gases were measured and analysed, a correction being made for any nitrogen which had not been displaced.

The mean sp. gr. found was 1·265, whilst the value calculated from $F = 19$ is 1·316. C. H. B.

Autoxidation. By M. TRAUBE (*Ber.*, **22**, 3057—3062; compare Abstr., 1889, 937).—A reply to Hoppe-Seyler (Abstr., 1889, 1106) The author is satisfied that he has proved that nascent hydrogen in presence of oxygen molecules has not a powerful oxidising action, as stated by Hoppe-Seyler, and also that the oxidising action of palladium

hydride cannot be attributed to nascent hydrogen. He criticises Hoppe-Seyler's remarks very severely, and concludes by expressing the hope that his part in the discussion on antoxidation with Hoppe-Seyler may be ended. F. S. K.

Hydrogen Arsenide and Antimonide. By O. Brunn (*Ber.*, **22**, 3202—3207).—Hydrogen arsenide and hydrogen sulphide do not act on one another in absence of air at the ordinary temperature, either in the gaseous condition or in aqueous solution, even on exposure to direct sunlight. The admission of air quickly causes in both cases a precipitate of arsenious sulphide. It has been previously observed that hydrogen arsenide is itself acted on by air or oxygen, with formation of a black powder. An examination of this product has shown that its composition varies with the amount of air present, the gas being first oxidised to solid hydrogen arsenide, and then, if there be sufficient oxygen, to metallic arsenic. The above-mentioned formation of arsenious sulphide is, therefore, probably preceded by the formation of arsenic.

If the mixture of hydrogen arsenide and sulphide is heated, separation of arsenious sulphide commences at about 230°. Separate experiments with hydrogen arsenide show that the latter commences to dissociate at 230°, and that in this case also the formation of arsenious sulphide is a secondary reaction.

Hydrogen antimonide is at once decomposed by hydrogen sulphide, even in absence of air and light. On heating the former gas alone, dissociation commences at about 150°. The author proposes to make use of this fact for the detection of traces of antimony occurring together with arsenic, in other gases, such as hydrogen. For this purpose the gases are passed through a tube 0·8—1·0 metre in length, and heated by a liquid boiling at 208—210°. No arsenic whatever is deposited, and the antimony mirror may be further examined by the usual methods. H. G. C.

Combination of Sodium and Potassium with Ammonia. By A. Joannis (*Compt. rend.*, **109**, 900—902).—When one equivalent of the alkali metal is brought in contact with 20 equivalents of liquid ammonia, and the ammonia gas is afterwards removed, its pressure rapidly diminishes. At a certain point, the pressure becomes constant; in the case of sodium the pressure was 1700 mm. at 0°, and the composition of the mixture $Na + 5·3NH_3$. The exact composition varies with the temperature, notwithstanding the constancy of the pressure, and hence the product in the tube is not a definite compound. When a further quantity of the gas is removed, a solid substance with an intense copper-red colour is left, and the constant pressure observed may be regarded as the vapour pressure of liquid ammonia saturated with this solid. When only one molecule of ammonia is present for each atom of metal, no trace of liquid remains, and if still more ammonia is removed, the free sodium or potassium alone remains, and as this decomposition takes place at a constant pressure, it may be regarded as true dissociation. Careful experiments gave 0·99 equivalent as the inferior limit, and 1·1 equivalent as the superior limit of the quantity of ammonia combined with one atom of the alkali metal, and

it may therefore be taken that the solid residue, which the author calls *potassammonium* or *sodammonium*, has the composition NH_3K or NH_3Na. C. H. B.

Thiosulphates. By A. Fock and K. Klüss (*Ber.*, **22**, 3096—3101). —Potassium thiosulphate, $3K_2S_2O_3 + H_2O$, separates in colourless, prismatic crystals when an aqueous solution of the salt is evaporated over sulphuric acid, and when the mother liquors are kept over sulphuric acid for some time longer the salt separates in large, rhombic crystals, with 5 mols. H_2O; these results agree with those previously obtained by Rammelsberg, Kessler, and Döpping.

Lithium thiosulphate, $Li_2S_2O_3 + 3H_2O$, crystallises in large, colour less, very deliquescent needles, and is soluble in alcohol; when heated, it is decomposed into lithium sulphate and lithium sulphide.

Ammonium thiosulphate, $(NH_4)_2S_2O_3$, separates in anhydrous, colourless plates when an aqueous solution of the salt is evaporated over sulphuric acid; Rammelsberg found that the salt crystallised with 1 mol. H_2O. F. S. K.

Allotropic Forms of Silver. By M. C. Lea (*Amer. J. Sci.* [3], **37**, 476—491; and **38**, 47—50, and 129).—The author considers that his own researches have established the existence of silver subchloride, although the experiments of Newbury, Muthmann, v. Pfordten, and others, have shown that there is at present no evidence of the existence of a silver sub-oxide, Ag_4O. He points out that the fact that a substance will not pass through a dialyser merely proves that it is colloïdal and not that it is not in solution. Further, many substances which undoubtedly form true solutions are carried down by gum when the latter is added to the liquid and then precipitated by addition of alcohol. The products described in these papers differ from those obtained by v. Pfordten in that they readily amalgamate with mercury and evolve no gas when treated with dilute sulphuric acid.

Silver can exist in three allotropic forms, or more probably in three modifications of the same form, the differences between the three being less than their differences from normal silver. They differ in colour and other physical properties, and in chemical activity; they probably represent an active condition of silver of which the ordinary metal is a polymeride. The three modifications are as follows:—

A. *Soluble allotropic silver*, which forms a deep-red solution, is matt black, blue, or green, when solid and moist, and brilliant metallic bluish-green when dry.

B. *Insoluble allotropic silver*, derived from the preceding modification, dark reddish-brown when moist, and brilliant metallic bluish-green, like A, when dry.

C. *Gold-like allotropic silver*, dark-bronze coloured when moist, but like burnished gold when dry. No soluble modification of this form seems to exist, but a copper-coloured variety is produced under certain conditions.

All three modifications have certain properties in common. When dry they are very friable and are readily reduced to an impalpable

powder, differing markedly in this respect from normal silver. Their most striking property, however, is their power of drying with their particles in optical contact, and if spread while moist on paper or glass, they form mirrors of great perfection and beauty when dry. If these films are treated with solutions of the haloids, ferric chloride, or, best of all, sodium hypochlorite, very beautiful interference colours are obtained. The phenomena are quite different from those obtained with normal silver leaf under the same conditions. Very dilute mineral acids and moderately dilute acetic acid immediately convert allotropic silver into grey normal silver without the evolution of any trace of gas.

A. *Soluble allotropic silver* is obtained by the action of concentrated solutions of ferrous citrate or a mixture of ferrous sulphate and sodium citrate on a concentrated solution of a silver salt. If the solutions are not very concentrated, a deep-red liquid is formed which may remain transparent for some time or may gradually deposit a black precipitate. Concentrated solutions should be used, the following proportions being found to give the best results. A mixture of 200 c.c. of a 30 per cent. solution of ferrous sulphate and 280 c.c. of a 40 per cent. solution of sodium citrate was added at once to 200 c.c. of a 10 per cent. solution of silver nitrate. The liquid, which immediately becomes black, is vigorously agitated for several minutes, allowed to remain for 10 to 15 minutes, and the liquid then decanted. A large quantity of a lilac-coloured precipitate remains, but alters slowly even in contact with the mother liquor, and when it is drained the colour changes almost immediately to deep blue. It may be washed with a solution of sodium or ammonium citrate, sulphate, or nitrate, preferably ammonium nitrate, because, although completely soluble in pure water, it is quite insoluble in presence of 5 to 10 per cent. of these salts. A good plan is to add sufficient water to dissolve nearly the whole of the precipitate and then sufficient ammonium nitrate to reprecitate it. The substance gradually changes whilst being washed and becomes less and less soluble. After washing seven or eight times in the manner described, it was washed with alcohol of 95 per cent. to remove ammonium nitrate and then analysed: it contained 97·27 per cent. of silver and the filtrate from the silver chloride precipitate contained only ferric citrate. It retains water even after prolonged exposure in a dry vacuum, but becomes anhydrous at 100°; at low redness it gives off small quantities of carbonic anhydride, but no trace of either hydrogen or oxygen. These determinations were made after the substance had become insoluble, and hence it seemed possible that while in solution it might be combined with citric acid. Determinations of the silver and citric acid in a solution of the purified substance (which was proved by optical examination to form a true solution) gave the ratio of silver to citric acid in one case as 55·63 : 1 and in another 193·7 : 1, results which show that the proportion of citric acid is variable and is always very small. Some of the purified precipitate was dried at 100°, mixed with water, and again evaporated to dryness; all the silver separated as grey normal silver and the liquid was quite neutral. If a perfectly neutral iron solution is used in the prepara-

tion of the substance, the liquid after reduction is either neutral or very faintly acid. If a solution of the purified lilac precipitate is mixed with a neutral solution of magnesium sulphate, the insoluble form, which consists of almost pure silver, is thrown down, but the liquid remains quite neutral. Possibly the silver is in combination with some neutral substance derived from citric acid, but if so, it must be some entirely new compound. Ballo has observed that the action of ferrous salts on tartaric acid produces a neutral substance of the same composition as arabin, $C_6H_{10}O_5$. The change which the lilac precipitate undergoes during purification and washing is indicated by changes of colour, and the constitution of the lilac precipitate whilst under the mother liquor is still doubtful. If the precipitate is spread on paper, it is blood red while moist, blue with metallic lustre when half dry, and matt blue when quite dry. If dried in lumps, the colour and lustre vary considerably.

B. *Insoluble allotropic silver* is obtained from the preceding form by spontaneous change or by the action of certain salts. Alkaline sulphates, nitrates, and citrates precipitate soluble allotropic silver from its solutions, but it still remains soluble. Magnesium, copper, iron, and nickel sulphates, potassium dichromate, potassium ferrocyanide, barium nitrate, and silver nitrate all precipitate it in an insoluble form. The soluble precipitate is blue or bluish-black; the insoluble form is brown and continually darkens while being washed. Ammonia dissolves the insoluble modification; sodium borate and alkaline sulphates reconvert it into a soluble form, different however from the original. With a dilute solution of sodium borate, a brown solution is obtained; with sodium or potassium sulphate, a yellow-red solution; with ammonium sulphate, a red solution. If concentrated solutions of these salts are used, the change into the soluble form takes place, but the substance does not dissolve until the salt has been washed away by pure water. Sodium nitrite added to a solution of the soluble form partially converts it into normal silver and renders it quite insoluble even in ammonia. In one case the insoluble variety became spontaneously soluble and formed a rose-red solution. In another case it separated very slowly and spontaneously from a solution in the form of short, black needles and thin prisms, which lost their crystalline form in contact with pure water but did not dissolve; it dried with a green, metallic lustre. It seems that pure water tends to produce a colloïdal form, whether soluble or insoluble, whilst salts tend to produce a crystalline form.

Analysis showed that the insoluble allotropic silver contained 97·96 per cent. of the metal, the remainder being ferric citrate. It retains water in a vacuum but becomes anhydrous at 100°.

When spread in the moist state over paper, it forms a green film with a brilliant metallic lustre. The green is a mixture of blue and yellow, one or the other predominating according to the direction of the illumination. The yellow is polarised in the plane of incidence, and the blue in a direction normal to that plane. All the products were more or less yellow, but the proportion of blue light varied considerably and is less the more prolonged the washing of the precipitate. If some of the substance is precipitated by means of

magnesium or aluminium sulphate and is spread on paper without washing, the dry film has the appearance of a highly lustrous, bright-blue metal. When the moist substance is spread on glass, it forms very perfect mirrors when dry.

C. *Gold-like allotropic silver* is obtained by the reduction of silver tartrate by ferrous tartrate in dilute solutions, but the permanency of the product depends on the details of the preparation and is greater the more completely air and light are excluded from the dry substance. The following method gives a permanent product:—a mixture of 107 c.c. of a 30 per cent. solution of ferrous sulphate, 200 c.c. of a 20 per cent. solution of sodium-potassium tartrate, and 800 c.c. of water is added gradually, and with constant stirring, to a mixture of 200 c.c. of a 10 per cent. solution of silver nitrate, 200 c.c. of the solution of the alkaline tartrate, and 800 c.c. of water. The precipitate is at first red, but changes to black, and when washed on the filter becomes bronze-coloured. If dried in lumps or in films on paper or glass, it has the colour and lustre of burnished gold. On glass it forms very perfect mirrors. It is very permanent when dry, but more liable to change while moist, and forms a copper-coloured variety, which however is still bright and permanent. While washing, it is important to keep the filter full of water. This modification contains 97·8 to 98·75 per cent. of silver, the remainder being ferric tartrate.

The specific gravities of B and C were determined after they had been left under water in a vacuum for a long time; sp. gr. of insoluble allotropic silver = 9·58; sp. gr. of gold-like allotropic silver = 8·51. The sp. gr. of normal silver is 10·5, and that of finely divided precipitated silver 10·62.

At 100°, a bluish-green film of B acquired a superficial bright-yellow colour, and a film of C under the same conditions became superficially blue, but these changes were confined to the surfaces.

All three modifications are affected by light; A and B become brown after some hours, and the coppery modification of C becomes bright-yellow. A very bright bluish-green modification of B obtained by rapid and short washing acquired the colour of gold after one day's exposure to sunlight; samples which have been well washed yield a matt film on paper and become brown when exposed to light.

The gold-like modification acquires a somewhat purer yellow colour when exposed to light in absence of moisture, but in presence of moisture 3 or 4 days exposure to sunlight changes it into white normal silver of great beauty. Moisture alone tends to darken its colour. It is interesting to note that organic compounds of silver always yield grey or black, lustreless products when exposed to light.

The modifications A and B are obtained by the reduction of silver citrate by ferrous citrate, and C by the reduction of silver tartrate by ferrous tartrate. No similar results are obtained by the action of ferrous oxalate on silver oxalate. C. H. B.

Action of Light on Silver Chloride. By R. HITCHCOCK (*Amer. Chem. J.*, 11, 474—480).—Finely divided precipitated silver chloride was allowed to settle on microscopic cover glasses,

carefully washed, and dried in a desiccator. In this way the thin glass slips are obtained covered with a very thin, semi-transparent layer of silver chloride. They were then weighed, placed in a tube through which a current of pure hydrogen was passing, and exposed to sunlight, the chlorine which was liberated being absorbed in silver nitrate solution and afterwards weighed. The glass slips with the silver chloride were weighed after the experiment. The loss of weight varied from 0·042 to 0·049 gram per gram of silver chloride; the chlorine absorbed by the silver nitrate was very slightly smaller in quantity than the loss in weight of the silver chloride. In one case the product gave up a considerable proportion of silver when heated with dilute nitric acid, and hence it would seem that decomposition had gone so far that the protective action of the unaltered silver chloride had to a great extent been eliminated. C. H. B.

Zinc Hydrosulphide. By V. v. ZOTTA (*Monatsh.*, **10**, 807—812). —The author finds, contrary to the statement of Thomsen (Abstr., 1879, 206), that when equivalent quantities of zinc sulphate and an alkaline hydrosulphide are mixed, the precipitate obtained has not the formula $Zn(SH)_2$, but must be regarded as having the composition $Zn_3H_2S_4 = Zn(SH)_2,2ZnS$. The production of this compound explains the evolution of hydrogen sulphide which takes place on adding an alkaline hydrosulphide to zinc sulphate; for the compound $Zn_3H_2S_4$ may be regarded as being formed from 3 mols. of the hydrosulphide by loss of 2 mols. of hydrogen sulphide. Thomsen further says (*loc. cit.*) that if zinc sulphate is treated with two equivalents of sodium hydrosulphide, no precipitate is produced, but the resulting solution is slightly opalescent; and concludes that sodium hydrosulphide behaves towards zinc sulphate in precisely the same way as sodium hydroxide. The author in repeating this experiment finds that about 20 per cent. of the sulphur present is evolved as hydrogen sulphide, but that long continued boiling does not cause the formation of a precipitate. If, however, a mixture of zinc sulphate with four times its equivalent of sodium hydrosulphide is made, the slightly opalescent solution obtained is rendered turbid on boiling for a few minutes, or on treatment with acids, alkalis, or certain salts, and the precipitate is identical with the sulphide $Zn_3H_2S_4$, mentioned above. G. T. M.

Crystalline Anhydrous Zinc Phosphate and Zinc Arsenate. By A. DE SCHULTEN (*Bull. Soc. Chim.* [3], **2**, 300—302).—Zinc chlorophosphate did not separate from the solution of normal tetrahydrated zinc phosphate in fused zinc chloride, but rhombic prisms of anhydrous zinc phosphate were obtained from the melt; these have a sp. gr. of 3·998 at 15°, and melt at a red heat. The same substance is produced by heating the hydrated salt with a concentrated solution of zinc chloride in sealed tubes at 250°.

On evaporating to dryness arsenic acid solution containing excess of zinc chloride, and subsequently fusing the product, prismatic crystals of anhydrous zinc arsenate were obtained having a sp. gr. of 4·913 at 15°.

Hence, zinc differs from magnesium and cadmium in not forming chlorophosphates and chlorarsenates (compare Abstr., 1890, 11).

T. G. N.

Egyptian Blue. By O. MÜHLHÄUSER (*Dingl. polyt. J.*, **272**, 144). —This blue pigment was used by the Romans in the first few centuries of the Christian era. It is said to have been discovered by Vitruvius in Alexandria, who prepared it by intimately mixing finely divided sand with sodium carbonate, adding copper filings to the mixture, moistening with water, moulding into balls, drying, and heating in clay pots until the blue colour was produced.

Fouqué has recently examined this colouring matter, and finds that its composition is that of a double silicate of calcium and copper, $CaO,CuO,4SiO_2$. It has a sp. gr. of 3·04, and crystallises in laminæ belonging to the dimetric system. The crystals exhibit dichroism, showing a pale-red colour when viewed by reflected light, and a blue colour when the light is transmitted. The blue substance resists the action of most chemical agents, and this fact explains the perfect state of its preservation in the wall paintings executed about 1900 years ago. According to Fouqué, its preparation may be effected at a bright red heat from materials devoid even of traces of alkali. At a higher temperature the blue is decomposed into cuprous oxide, wollastonite and a light-green, vitreous mass; the higher the temperature, the more of the latter is formed, until eventually wollastonite disappears entirely. The same author finds the method described by Vitruvius applicable, but prefers the use of potassium sulphate as flux.

The brightness and fastness of this pigment, the fact that it resists atmospheric influences and is not affected by most chemical agents, as well as the facility and cheapness of production, render it desirable that its manufacture should be again taken up. D. B.

Nature of Steel. By KOSMANN (*Dingl. polyt. J.*, **270**, 190—192). The author reviews the theories of Rinman, Osmond and Werth, Müller, Ledebur, and Baedeker, respecting the state in which carbon exists in steel. He does not agree with the assumption that carbon exists evenly alloyed with iron only in hardened steel, whilst in slowly-cooled steel it is dissolved by the iron in the form of the compound Fe_3C, but considers that in rapidly-cooled steel the carbon is also chemically combined with the iron. D. B.

Synthesis of Double Sulphides of the Alkali Metals and the Heavy Metals. By H. BRUNNER (*Chem. Centr.*, 1889, ii, 554—555; from *Arch. sci. phys. nat. Genève*, **22**, 68—69).—The author has succeeded in preparing the double sulphides of sodium and the metals of the iron-group by heating the oxalate of the heavy metal with sodium thiosulphate. *Sodium iron sulphide* crystallises in beautiful, bronze-red prisms; *chromium sodium sulphide* is a reddish-brown mass; whilst *manganese sodium, cobalt sodium,* and *nickel sodium sulphides* form lustrous, yellow, crystalline masses, readily oxidised on exposure to the air. These double sulphides are also formed when the alkaline carbonates are calcined with sulphur and the oxalate of the heavy

metal. The chromium sodium sulphide is also obtained by heating the double oxalate with sulphur. J. W. L.

Nickeloxydiamine Nitrite. By L. SORET and F. ROBINEAU (*Bull. Soc. Chim.* [3], 2, 138).—To prepare this salt, ammonia solution of sp. gr. 0·924 (3 kilos.) and sodium nitrite (1 kilo.) are added to nickel sulphate (1 kilo.) dissolved in boiling distilled water (1 litre); the mixture is placed aside for 4—5 days, and the resulting crop of crystals, after washing, is recrystallised from a hot ammoniacal solution. Although the nickel salt used contained 3 per cent. of cobalt, the crystals of nickeloxydiamine nitrite produced were absolutely pure. T. G. N.

Double Fluorides of Antimony. By G. STEIN (*Chem. Zeit.*, **13**, 357).—By evaporating solutions of antimonious fluoride with lithium chloride or fluoride, the respective double salts $SbF_3,LiCl$ or SbF_3,LiF are obtained; they crystallise in hexagonal tables; both are readily soluble in water without decomposition, the former being the more soluble; the solutions have a slightly acid reaction. Ammonia precipitates flocculent, gelatinous antimonious oxide from these solutions; whereas the known double fluorides of antimony yield heavy precipitates.

In mordanting experiments with tannin-aniline colours, 100 grams of potassium antimony tartrate, or 60 grams of lithium antimony fluoride, or 65 grams of lithium antimony chloride were employed, and the results obtained as regards the purity and beauty of colour were of equal value.

Antimony fluoride does not form any useful double salts with potassium, sodium, or ammonium thiocyanate; in fact, the thiocyanate decomposes, and especially with ammonium thiocyanate the solution of the double salt, when strongly evaporated, gives a precipitate of antimony sulphide. D. A. L.

Antimonates. By F. EBEL (*Ber.*, **22**, 3044—3045).—The author has prepared the following compounds by adding excess of a concentrated solution of the metallic salt to a boiling aqueous solution of sodium antimonate ($Na_2H_2Sb_2O_7 + 7H_2O$):—Barium antimonate, $BaSb_2O_6 + 5H_2O$; Beryllium antimonate, $BeSb_2O_6 + 6H_2O$; silver antimonate, $Ag_2Sb_2O_6 + 3H_2O$; copper antimonate, $CuSb_2O_6 + 5H_2O$; cadmium antimonate, $CdSb_2O_6 + 6H_2O$; lead antimonate, $PbSb_2O_6 + 5H_2O$; zinc antimonate, $ZnSb_2O_6 + 5H_2O$; manganese antimonate, $MnSb_2O_6 + 5H_2O$; amorphous cobalt antimonate, $CoSb_2O_6 + 6H_2O$; the crystalline salt, $CoSb_2O_6 + 12H_2O$; amorphous nickel antimonate, $NiSb_2O_6 + 6H_2O$; the crystalline salt, $NiSb_2O_6 + 12H_2O$; the ferric salt, $Fe_2O_3,Sb_2O_5 + 7H_2O$; and the aluminium salt, $Al_2O_3,Sb_2O_5 + 9H_2O$. F. S. K.

Behaviour of Bismuth with Sulphur and Selenium. By P. A. v. SCHERPENBERG (*Chem. Centr.*, 1889, ii, 643—644; from *Mitt. pharm. Inst. Erlangen*, 2 Heft, 1—12).—The author has not succeeded in preparing a higher sulphide of bismuth than the trisulphide,

although an oxysulphide, Bi_2O_3S, is formed when bismuth pentoxide, suspended in boiling benzene, is treated with dry hydrogen sulphide.

Attempts to prepare double sulphides, similar to those described by Schneider (*Ann. Phys. Chem.*, **91**, 404), but with a larger proportion of sulphur, by heating the pentoxide with concentrated potassium hydrosulphide solution in a sealed tube, only resulted in the formation of the lower oxide. If, however, the pentoxide is fused with potassium polysulphide, the compound $Bi_2S_3.K_2S$ remains as a crystalline mass.

With selenium, the double salt Bi_2Se_3,K_2Se may be prepared in like manner.
J. W. L.

Platinum Tetrafluoride. By H. MOISSAN (*Compt. rend.*, **109**, 807—809).—Fluorine, free from hydrogen fluoride, does not attack platinum below 100°, and combination does not take place readily below 500—600°. In presence of hydrogen fluoride, the reaction takes place far more easily, even in the case of liquid hydrogen fluoride saturated with fluorine. Platinum tetrafluoride is obtained by heating a bundle of platinum wire to dull redness in a thick platinum tube or a fluor-spar tube through which a current of fluorine is passed. As soon as combination is complete, the product is transferred to a perfectly dry tube. It forms a deep-red, fused mass or chamois-yellow crystals resembling anhydrous platinum tetrachloride, is extremely hygroscopic, and cannot be kept for a long time even in a well-corked and carefully-dried tube. When thrown into a small quantity of water, a tawny coloration is first produced, then heat is rapidly developed, and decomposition takes place with formation of hydrogen fluoride and hydrated platinum dioxide. Very dilute solutions are more stable, but the same change takes place immediately if the liquid is heated. This reaction explains Fremy's failure to obtain platinum tetrafluoride by the action of hydrofluoric acid on hydrated platinum dioxide.

When platinum fluoride is heated, it yields fluorine and metallic platinum, the latter being left in a crystalline form, a result which supports Daubrée's views on the mineralising effect of fluorine.
C. H. B.

Mineralogical Chemistry.

Composition of Roumanian Rock-salt. By ISTRATI (*Bull. Soc. Chim.* [3], **2**, 4—8).—This mineral, which is mined in the Carpathians, contains 98—99·8 per cent. of sodium chloride. Some varieties have a definite odour of petroleum, which in some cases is contained in the mineral to such an extent that explosions have occurred. The variety known as "puturosa" contains as much as 117 c.c. of gases per kilo.; the gas obtained from Dolftana salt yielded on analysis 25 per cent. of unsaturated hydrocarbons and 19·6 per cent. of oxygen, but no carbonic anhydride.
T. G. N.

Kobellite from Colorado. By H. F. KELLER (*Zeit. Kryst. Min.*, **17**, 67—72).—This mineral, from the Silver Bell mine, Ouray, is fine-grained, somewhat fibrous, and exhibits no crystalline form. It has a sp. gr. of 6·334. The analyses lead to the formula $2(PbAg_2Cu_2)S,(SbBi)_2S_3$. This does not agree with Rammelsberg's formula, Pb_3BiSbS_6. The mean of four analyses was as follows:—

S.	Bi.	Sb.	Pb.	Ag.	Cu.	Fe.	Zn.	Gangue.	Total.
18·39	28·40	7·55	36·16	3·31	2·59	1·50	0·39	0·45	98·74

B. H. B.

Aurichalcite. By A. BELAR (*Zeit. Kryst. Min.*, **17**, 113—127).—In the aurichalcite of Temperino, Delesse detected the presence of calcium. Other chemists regard this as merely a mechanical impurity in the material analysed, and believe that aurichalcite is nothing more than a compound of copper and zinc hydrated carbonates. Analyses were made of aurichalcite (1 and 2) from Moravicza, (3) from Campiglia, and (4) from Sardina, with the following results:—

	CuO.	ZnO.	Fe_2O_3.	H_2O.	CO_2.
1	20·39	54·70	—	13·53	11·38
2	21·43	53·57	—	26·78	
3	20·20	55·51	—	26·50	
4	15·58	58·72	2·17	22·97	

All four analyses lead to the formula $CuCO_3 + 3Zn(HO)_2$.

In conclusion, the author gives the results of experiments made with the view of preparing aurichalcite artificially. He finds that the statement of Delesse, that aurichalcite re-crystallises out from solutions of the mineral in ammonium carbonate, is not correct.

B. H. B.

Messelite, a New Mineral. By W. MUTHMANN (*Zeit. Kryst. Min.*, **17**, 93—94).—This mineral forms radiated masses of brown or colourless tablets in a bituminous shale embedded in the lignite of the Messel mine in Hesse-Darmstadt. The crystals were found optically to be triclinic. Analysis gave the following results:—

P_2O_5.	CaO.	FeO.	MgO.	MnO.	H_2O.	Insol.	Total.
37·72	31·11	15·63	1·45	trace	12·15	1·40	99·46

These results correspond with the formula $(CaFeMg)_3(PO_4)_2 + 2\frac{1}{2}H_2O$. Messelite differs from fairfieldite by the absence of manganese and by the different proportion of water. B. H. B.

Mazapilite, Anhydrite, Eleonorite, &c., from North America. By G. A. KÖNIG (*Zeit. Kryst. Min.*, **17**, 84—92).—1. *Mazapilite* is the name given by the author to an extremely rare mineral from the Jesus Maria Mine, Mazapil, Mexico. The crystals belong to the rhombic system, the axial ratio being $a : b : c = 0·8616 : 1 : 9·9969$. Analysis gave—

As_2O_5.	Sb_2O_5.	P_2O_5.	Fe_2O_3.	CaO.	H_2O.	Total.	Sp. gr.
43·60	0·25	0·14	30·53	14·82	9·83	99·17	3·582

Formula: $Ca_3Fe_2(AsO_4)_4(OFe{\cdot}OH)_2 + 5H_2O$.

2. *Anhydrite.*—This mineral was found at the Darby tunnel, seven miles from Philadelphia, in the unusual form of crusts consisting of parallel prisms on the plagioclase and angite of a diabase. The silicates of the rock exhibited no trace of decomposition.

3. *Eleonorite from Arkansas.*—A strongly dichroic crystal in a geode of dufrenite, from Sevier Co., Arkansas, was identified by the author as Streng's eleonorite. As all the water was driven off at 280°, Streng's formula, $Fe_6P_4O_{19} + 8H_2O$, is preferable to that of Groth, $Fe_2(OH)_3(PO_4)_2 + 2\frac{1}{2}H_2O$.

4. *Minerals from Franklin, New Jersey.*—At this well-known locality the following minerals have recently been met with:—Chloauthite, arsenic-nickel, fluorspar, apatite, and hydrated nickel silicate; the latter on analysis gave—

SiO_2.	NiO.	CaO.	MgO.	ZnO.	FeO.	H_2O.	As_2O_5.	Total.
31·02	38·22	0·70	0·42	4·00	2·25	16·58	4·77	97·96

B. H. B.

Pseudobrookite, from Havredal, Norway. By A. CEDERSTRÖM (*Zeit. Kryst. Min.*, **17**, 133—136).—This mineral was first analysed by Koch and Lattermann. Owing to want of material, the analysis could not be made with accuracy. The discovery of large crystals at Havredal has enabled the author to make an analysis of carefully selected material, the results being as follows:—

	Author.	Koch.	Lattermann.	Calculated.
Ignition...	—	0·69	—	—
Fe_2O_3.....	56·42	42·29	48·64	56·54
TiO_2......	44·26	52·74	46·79	43·46
MgO	—	4·28	4·53	—
Total	100·68	100·00	99·96	100·00

The last column gives the percentage composition calculated from the formula $Fe_4(TiO_4)_3$. B. H. B.

Chemical-mineralogical Theories. By V. GOLDSCHMIDT (*Zeit. Kryst. Min.*, **17**, 25—66).—This memoir is divided into three sections: (1) on the varieties of isomorphism, (2) on symbols and formulæ, and (3) on the formulæ of the silicates. The two first sections serve as an introduction to the views propounded in the third. By the introduction of letters, the author endeavours to simplify the formulæ of silicates. Thus he employs the symbols—

E for R'_4O_2 or R''_2O_2, representing SiO_2,
A for $R'_2R^{vi}{}_6O_4$, representing Si_2O_4,
R_2 for $R^{vi}{}_2O_6$, representing Si_3O_6,
Si for SiO_2,
Si_2 for Si_2O_4, &c.,

so that, for example, $\frac{ASi_2}{Si_4}$ would be the abbreviated formula for albite. Further, he employs symbols for the silicate molecules of more frequent occurrence; thus the hornblende molecule is $H = ASi = \left.\begin{matrix} R'_2R \\ Si \end{matrix}\right\} O_6$, and the nepheline molecule $N = ASi_2$.

B. H. B.

Artificial Preparation of Wollastonite. By E. HUSSAK (*Zeit. Kryst. Min.*, **17**, 101).—In these experiments, a glass composed of $3(Na_2O,SiO_2) + 2(CaO,B_2O_3)$ was melted, and, on cooling, was found to be free from bubbles, crystals, and crystallites. Mixed with $CaSiO_3$ (1 mol.), the mass on cooling was found to be full of bubbles and fissures, and on the sides of the crucible there were a few imperfect, columnar, colourless, minute crystals. When more $CaSiO_3$ (2 mols.) was added, the colourless columns increased in number, and formed into a radiated globule. The mixture of the glass and 3 mols. of $CaSiO_3$ on cooling became completely crystalline. A number of hexagonal tablets were present, but the minute columns still predominated. The tablets belong to the hexagonal, optically positive calcium silicate, whilst the columns are crystals of wollastonite extended in the direction of the axis of symmetry. B. H. B.

Leucitophyre from Persia. By V. STEINECKE (*Zeit. Kryst. Min.*, **17**, 110—111; from *Zeit. Naturwiss.*, **60**, 4).—At Koschkserai Maraud, in a magma of orthoclase, plagioclase, nepheline, augite, leucite, and magnetite, there are found crystals of leucite, augite, olivine, sanidine, and nepheline. The leucite gave on analysis—

SiO_2.	CaO.	MgO.	MnO.	Al_2O_3.	Fe_2O_3.	K_2O.	Na_2O.	Ignition.
54·54	0·99	0·25	trace	22·14	1·74	19·83	0·71	1·33

An analysis of the augite is also given. B. H. B.

Nosean-bearing Ejections from the Laacher See. By L. L. HUBBARD (*Zeit. Kryst. Min.*, **17**, 208; from *Tschermak's min. Mitth.*, **8**, 356—399).—In the ejections found at the Laacher See, nosean is principally confined to geodes, and in its formation in a trachytic rock, sanidine has, in many cases, been produced. The latter occurs in radiated masses, and gave on analysis the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	Total.	Sp. gr.
65·36	21·19	0·45	0·56	trace	6·77	5·72	100·05	2·556

B. H. B.

Wiluite. By R. PRENDEL (*Zeit. Krys. Min.*, **17**, 94—97).—The author has made an exhaustive investigation of the physical properties of the idocrase of Wilui, and proves that this so-called wiluite differs considerably from idocrase proper. B. H. B.

Two Analyses of Mica. By A. BECKER (*Zeit. Kryst. Min.*, **17**, 128—132).—The author has analysed (1) biotite and (2) muscovite of remarkable purity, carefully isolated from the gneiss, 338 metres

below the surface, at a mine at Halsbrücke, near Freiberg, in Saxony. The analytical results were as follow :—

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	K_2O.
1....	34·70	4·58	17·17	2·11	19·05	0·50	9·52	8·91
2....	46·74	1·52	32·56	1·55	0·92	—	1·18	10·37

	Na_2O.	H_2O.	F.	Total.
1	1·24	3 56	0·20	101·54
2	1·02	3·55	—	99·41

The formulæ of the two minerals are—

(1) $5(KNaH)_4SiO_4 + 8(FeMnMg)_2SiO_4 + 3(Al_2Fe_2)_2(SiO_4)_3$.
(2) $2(KNaH)_2SiO_3 + (Al_2Fe_2)_2(SiO_4)_3$. B. H. B.

Chemical Composition of Vesuvian. By J. H. Vogel (*Zeit. Kryst. Min.*, **17**, 215—216).—The author gives the results of analyses of nine specimens of vesuvian from different localities :—1. Cziklowa, yellowish-green crystals, sp. gr. 3·38, directly determined water 1·53 per cent.; 2. Becco della Corbassera, Ala, yellowish-green masses, sp. gr. 3·386, H_2O 1·11 ; 3. Canzocoli, near Predazzo, large, yellowish-brown crystals, sp. gr. 3·404, H_2O 1·57 ; 4. Zermatt, dark-brown crystals, sp. gr. 3·488, H_2O 1·05 ; 5. Egg, sp. gr. 3·406 ; 6. Haslan, dark-brown masses, sp. gr. 3·419 ; 7. Sandford, brown crystals, sp. gr. 3·419 ; 8. Eker, sp. gr. 3·328 ; 9. Arendal, large, dark-brown crystals, sp. gr. 3·38.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
SiO_2	37·00	37·18	36·29	37·49	36·68	36·96	37·49	36·99	36·81
TiO_2	0·12	0·40	—	1·20	0·41	1·35	—	0·89	0·28
Fe_2O_3	1·53	2·94	3·85	4·68	2·62	2·43	2·79	3·46	3·92
FeO..........	0·83	0·62	1·23	1·09	2·76	2·47	3·08	1·51	2·21
Al_2O_3	17·51	17·12	16·31	14·74	16·70	16·18	16·03	15·43	16·25
CaO	35·56	34·35	36·01	35·43	34·97	35·11	33·84	35·81	35·49
MnO	trace	trace	—	trace	trace	trace	0·37	trace	0·14
MgO	3·82	3·56	2 70	2 42	2·51	2·67	2·13	3·04	2·72
K_2O	0 02	0·36	0·23	0 66	0·25	0·12	0·16	0·18	0·16
Na_2O	0·51	0·29	1·36	0·18	1·18	1·25	1·83	0·81	0·52
F	trace	trace	trace	trace	1·32	1·70	1·92	1·35	1·36
Ignition	2 61	2·99	3·41	2·78	1·15	0·86	1·25	0·87	0·98
Total	100·51	100·81	101·39	100·67	100·55	101·10	100·89	100·34	100·84

B. H. B.

Petrography of South-West Africa. By H. Wulf (*Zeit. Kryst. Min.*, **17**, 199—200; from *Tschermak's min. Mitth.*, **8**, 193—238).—The author gives analyses of scapolite from the scapolite-gneiss of the copper mine, and of Husab on the Tsoachaub, to the east of Wallfisch Bay. Analyses are also given of augite from the same rock, of wollastonite from the wollastonite-augite-gneiss of Reed, and from

the wollastonite-diopside rock of the copper mine. Epidote from Diepdal gave on analysis the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	Ignition.	Total.	Sp. gr.
37·04	22·99	14·19	trace	24·09	2·16	100·47	3·40

B. H. B.

Meteorite from Phu-Hong. By S. MEUNIER (*Compt. rend.*, **109**, 875—878).—This meteorite fell on September 22nd, 1887, at Phu-Hong, in Cochin China. It has a granular and even oolitic fracture, which is of a violet-grey colour, and the polished surface gives Widmannstatt's figures. Under the microscope, it is seen to consist of a transparent matrix, with opaque ramifying filaments and irregular granules. The transparent portion consists of peridote and magnesium pyroxene; the needles are arranged in very numerous spheroidal masses or chondrites.

The sp. gr. of the meteorite at 12° is 3·601; 35·37 per cent. is magnetic; 29·62 per cent. is soluble in hydrochloric acid, and 35·12 is not attacked by the acid. The magnetic portion contains 91·22 per cent. of iron and 9·05 per cent. of nickel, with distinct traces of cobalt. The composition of the soluble and insoluble non-magnetic portions are given in the following table:—

	SiO_2.	MgO.	CaO.	Na_2O.	FeO.	Al_2O_3.	Cr_2O_3.	Mn.
Insoluble..	63·60	28·48	1·91	0·87	4·10	1·22	0·92	trace
Soluble ...	40·09	45·97	—	—	14·00	—	—	—

The meteorite belongs to the type *limerickite*, and the author discusses the claims of certain other meteorites and terrestrial rocks to be included in the same type. C. H. B.

Analysis of Water from the Roundwood Colliery. By J. F. CLEEVES and J. C. PLATTS (*J. Soc. Chem. Ind.*, **7**, 729).—The sample was taken at a depth of 500 yards from the surface, and at a distance of 1,800 yards from the bottom of the shaft. The temperature was 19°, and the sp. gr. 1·0622. Analysis gave the following results expressed in grams per litre:—

SiO_2.	Al_2O_3 and Fe_2O_3.	$BaCl_2$.	$MgBr_2$.	$MgCl_2$.	$CaCl_2$.	NaCl.	Totals.
0·129	0·019	0·292	0·413	5·087	22·850	67·351	96·141

Chlorine required..............	59·38
Chlorine found.................	59·50

The water contains a large amount of gases dissolved in it, prominent among them being marsh gas. D. B.

Organic Chemistry.

Constitution of Petroleum. By J. A. LE BEL (*Bull. Soc. Chim.* [3], 2, 305—307).—The author considered that normal paraffins might alone be present in petroleum, the occurrence of the secondary paraffins being due to isomeric change occurring during its manipulation. He found, however, after isolation of the amylenes from natural petroleum, and subsequent treatment with concentrated hydrochloric acid in the cold, that dimethylethyl chloride boiling at 86° was obtained, which proves the occurrence of other than normal paraffins in petroleum, and according to him negatives the fermentation theory of petroleum formation, since no fermentation is known which produces both classes of compounds at a time. T. G. N.

Diallyl Tetrabromides. By G. WAGNER (*Ber.*, **22**, 3056—3057).—The author has previously stated that diallyl is probably a mixture of two isomerides (compare Abstr., 1889, 226), a view which, if correct, would explain the existence of the two tetrabromides, $C_6H_{10}Br_4$. Ciamician and Anderlini (this vol., p. 20), in assuming that these two bromides are geometrically isomeric, have probably overlooked the author's previous paper. F. S. K.

Action of Hydrocyanic Acid on Calomel. By FOUQUET (*J. Pharm.* [5], **20**, 397—400).—The statement that corrosive sublimate is produced by the action of hydrocyanic acid on calomel is incorrect. Mercury is set free with the formation of mercuric cyanide and hydrochloric acid in equivalent quantities. The reaction is almost always incomplete; but it may be started again by neutralising the free hydrochloric acid. J. T.

Ammoniomercuric Cyanides. By R. VARET (*Compt. rend.*, **109**, 903—904).—Alcoholic ammonia is saturated with mercuric cyanide, a current of ammonia gas being passed through the liquid while solution is taking place. The solution is heated at 50° to 60°, again saturated with dry ammonia, and allowed to cool. After some time, it deposits transparent, prismatic needles of the compound $HgCy_2,2NH_3$, which become opaque and rapidly lose ammonia when exposed to the air. At 100°, it loses the whole of the ammonia in a few hours.

If concentrated aqueous ammonia is saturated with mercuric cyanide, mixed with more ammonia, and cooled, it yields long, white, prismatic needles of the compound $HgCy_2,2NH_3,\frac{1}{2}H_2O$; this readily loses water and ammonia on exposure to air, although it is more stable than the preceding compound. At 100°, it decomposes completely, and mercuric cyanide is left.

The compound $HgCy_2,NH_3$ is obtained in small, hard, transparent crystals by heating aqueous ammonia with a large excess of mercuric cyanide in a closed vessel at 40°. It dissolves in ammonia, alters when exposed to air, and loses all its ammonia at 100°. The action

of dry ammonia on finely-powdered mercuric cyanide yields a yellowish-white product of the composition $10HgCy_2,NH_3$.

If ordinary ammonia is saturated with mercuric cyanide, mixed with one-tenth its volume of ammonia solution, and cooled to 0°, it yields small, white crystals of the compound $HgCy_2,NH_3,\frac{1}{2}H_2O$, very soluble in aqueous or alcoholic ammonia, very unstable when exposed to air. At 100°, it loses the whole of its water and ammonia.

C. H. B.

Interaction of Haloïd Salts of Mercury and Zinc. By R. VARET (*Compt. rend.*, **109**, 809—812).—A concentrated solution of zinc bromide is added drop by drop to a boiling saturated solution of mercuric cyanide, with vigorous agitation. The greater part of the precipitate redissolves, but the liquid remains turbid. It is filtered and allowed to cool, when it deposits white crystals of the compound $Hg_2ZnBr_2Cy_4 + 8H_2O$, which alters little, if at all, on exposure to air, is somewhat soluble in water, and becomes anhydrous at 100° or in a vacuum. When the hydrated compound is heated, it loses water, blackens, and decomposes into mercury, cyanogen, mercuric bromide, and zinc carbonate. Nitric acid converts it into zinc nitrate, mercuric cyanide, and mercuric bromide, hydrocyanic acid being evolved. Dry ammonia expels the combined water, and forms a compound, $Hg_2ZnBr_2Cy_4 + 2NH_3$, which loses ammonia when exposed to air, and is decomposed by water.

That this compound has the constitution $ZnCy_2,HgCy_2,HgBr_2 + 8H_2O$, and is not a compound of mercuric cyanide with zinc bromide, is proved by the following facts. Potassium iodide added to the aqueous solution produces at first a precipitate of zinc cyanide, followed by a precipitate of mercuric iodide; and Berthelot has shown that potassium iodide combines with mercuric cyanide with liberation of heat, but has no action on zinc cyanide. Cupric sulphate liberates cyanogen, and produces a peach-blossom coloured precipitate of mercuric cupric bromo-cyanide.

The addition of zinc cyanide to a boiling concentrated solution of mercuric bromide yields the same compound, and it is evident that its formation limits the action between mercuric bromide and cyanide and zinc cyanide and bromide, whatever may be the arrangement of the atoms in the initial system.

C. H. B.

Mannose. By E. FISCHER and J. HIRSCHBERGER (*Ber.*, **22**, 3218—3224).—The mannose employed in these experiments was obtained from vegetable ivory nuts by a modification of Reiss' method (Abstr., 1889, 687), instead of by the oxidation of mannitol. Comparative experiments made with mannose from the latter source showed the complete identity of the two sugars. The method of preparation was as follows: Sifted ivory-nut shavings (1 part) were digested with 6 per cent. hydrochloric acid (2 parts) on the water-bath for six hours, filtered hot, the residue pressed and again extracted with water. The brown solution, after treatment with animal charcoal, was neutralised with caustic soda solution, and an excess of phenylhydrazine acetate added. The resulting hydrazone was puri-

fied and converted into mannose by the method previously described (Abstr., 1889, 481).

Mannonic Acid.—For the preparation of this acid, a solution of mannose (1 part) in water (5 parts) is mixed with bromine (2 parts) at the ordinary temperature, frequently shaken, and allowed to remain 24 hours after the bromine has dissolved. The latter is then eliminated in the usual manner, and the resulting solution of mannonic acid converted into the *phenylhydrazide*, $C_{12}H_{18}N_2O_6$, by Fischer and Passmore's method (this vol., p. 152); this forms small, colourless, brilliant prisms which melt at 214—216° with decomposition, are soluble in hot water, but sparingly in cold water or alcohol. It may also be obtained directly from ivory nuts in the following manner: The ivory-nut shavings are heated with 6 per cent. hydrochloric acid, and the solution treated with animal charcoal as previously described. The quantity of mannose in solution is determined by precipitating a known quantity with phenylhydrazine, and for every part of sugar found, 2 parts of bromine added to the solution. The whole is frequently shaken until all the bromine has dissolved, and then allowed to remain. After evaporating off the free bromine, the solution is nearly neutralised with lead carbonate, filtered, precipitated with lead acetate solution, and again filtered. The filtrate may be then converted into the hydrazide as before. The latter, after recrystallisation, is decomposed by boiling baryta-water, the liberated phenylhydrazine extracted with ether, and the boiling liquid exactly precipitated with sulphuric acid. The filtrate, on evaporation, leaves a syrup, which solidifies to a slightly brown, crystalline mass. This is extracted twice with a little alcohol, and the residual white compound recrystallised from this solvent. The crystals obtained form stellate groups of colourless needles, and have the composition $C_6H_{10}O_6$, and are therefore the *lactone* of mannonic acid; this melts at 149—153°, is readily soluble in water, but less so in alcohol. Its aqueous solution is dextrorotatory, $[\alpha]_D = 53{\cdot}81$, and has a neutral reaction, but quickly dissolves carbonates on boiling, forming salts of mannonic acid. The *calcium* salt, $(C_6H_{11}O_7)_2Ca + 2H_2O$, forms microscopic prisms. The *strontium* salt, with 3 mols. H_2O, crystallises from alcohol in small prisms. The *barium* salt has not yet been obtained crystalline.

Mannonic acid is oxidised by nitric acid to a bibasic acid, which differs from saccharic and metasaccharic acids, and seemingly also from isosaccharic acid. This compound is undergoing further examination.

The authors have previously stated that mannose undergoes fermentation with yeast, and they have been able to confirm this by a repetition of the experiment with larger quantities. A 5 per cent. solution, when mixed with fresh yeast at the ordinary temperature, evolves carbonic anhydride in 10—15 minutes, and in 24 hours the reaction is complete. From the filtered solution, ethyl alcohol can be separated by fractional distillation, the yield seemingly being the same as that from dextrose. The liquid obtained by boiling ivory nuts with 6 per cent. hydrochloric acid also ferments after neutralisation with lime, although more slowly. As from 900—1000 tons

of such shavings are obtained yearly, and these yield 33 per cent. of their weight of sugar, it would seem that a commercial process for the preparation of alcohol from this source might be successfully founded.

Mannose is acted on by acetic chloride in exactly the same manner as dextrose. The *acetochloromannose* obtained likewise forms a syrup, which is sparingly soluble in water, but is decomposed by long-continued boiling with the latter into mannose and acetic and hydrochloric acids.
H. G. C.

Sugar from the Quebracho. By C. TANRET (*Compt. rend.*, **109**, 908—910).—The bark of the quebracho (*Aspidosperma quebracho*) yields a sugar, *quebrachite*, of the composition $C_7H_{14}O_6$, which crystallises from alcohol in anhydrous, rhomboidal prisms with a very sweet taste. It is very soluble in water, and somewhat soluble in boiling alcohol, but insoluble in ether. It melts at 186—187°, boils in a vacuum, and condenses in beautiful needles; rotatory power $[\alpha]_D = -80°$; sp. gr. at 0° = 1·54. Quebrachite ferments only in contact with beer-yeast, and has no action on Fehling's solution, but reduces ammoniacal silver nitrate. It is not affected by boiling dilute solutions of acids or alkalis, and gives no precipitate with basic lead acetate, but is precipitated by ammoniacal lead acetate provided the solution is not very dilute. Monohydrated sulphuric acid dissolves it readily, especially at 100°, with slight discoloration, forming *quebrachisulphuric acid*, a lævogyrate acid which yields soluble, non-crystallisable barium and calcium salts. When heated with acetic anhydride and zinc chloride, it yields a crystalline derivative which melts at 89°. With nitric and sulphuric acids, it yields an unstable nitrin, and when heated with nitric acid it gives rhodizonic acid.

When heated with hydriodic acid, quebrachite yields methyl iodide and an inosite which crystallises from alcohol in very brilliant, slender, efflorescent, prismatic needles, soluble in 2·3 parts of water at 12°, very slightly soluble in boiling alcohol, and insoluble in ether. It melts at 238°, is somewhat less volatile than quebrachite, and has a lævorotatory power of $[\alpha]_D = -55°$. With nitric acid it gives the inosite reaction.
C. H. B.

Formation of Raffinose. By F. HERLES (*Chem. Centr.*, 1889, ii, 421—422; from *Böhm. Zeit. Zucker-Ind.*, **13**, 455).—The author has subjected cane-sugar to the action of calcium hydroxide at various temperatures, but without being able to detect any formation of raffinose, a result in agreement with that obtained by Cech (*Chem. Centr.*, 1889, i, 682). He draws the conclusion that the formation of raffinose takes place in the beetroot. He also confirms the correctness of Herzfeld's statement (*ibid.*, 404), that it is formed by freezing the beetroot. The author finds that the preservation of the beetroot for too long a time favours the formation of raffinose.
J. W. L.

Melitriose and Melibiose. By C. SCHEIBLER and H. MITTELMEIER (*Ber.*, **22**, 3118—3124; compare Abstr., 1889, 953).—Melitose, prepared from cotton-seed meal exactly as described by Berthelot

(*Compt. rend.*, **103**, 533), is not changed by boiling baryta-water, does not reduce Fehling's solution, and crystallises unchanged from alcohol. Berthelot's statement (*loc. cit.*) that melitose is decomposed by alcohol into raffinose and eucalyn is, therefore, incorrect, and melitose is identical with raffinose.

When melitriose is treated with a dilute solution of invertin at the ordinary temperature for two hours, it is decomposed into melibiose and levulose; but when it is kept for 36 hours at 40° with a concentrated solution of invertin, it is decomposed into dextrose, galactose, and levulose; Berthelot's eucalyn is, therefore, identical with melibiose.

When melibiose is reduced with sodium-amalgam at the ordinary temperature, the solution being kept as neutral as possible, it is converted into a substance (*melibiotite*) which does not reduce Fehling's solution, but if a little of the solution is boiled for a short time with a few drops of sulphuric acid, it acquires powerful reducing properties, galactose being one of the decomposition-products of melibiotite. F. S. K.

Molecular Weights of Maltose and of several Inulin-like Substances. By Å. G. Ekstrand and R. Mauzelius (*Chem. Centr.*, 1889, ii, 444; from *Vetensk. Akad. Förhandl.* 1889, 157).—The molecular formulæ given below were determined by Raoult's method:—Anhydrous maltose, $C_{12}H_{22}O_{11}$. Triticin, $C_{36}H_{60}O_{30}$, from the root of *Dracæna rubra*, melts at 140°, and has the specific rotation $[\alpha]_D = -36·61$. Triticin, from *Triticum repens*, melts at 160°, and has the specific rotation $[\alpha]_D = -41·07$. Graminin, $C_{48}H_{80}O_{40}$, from *Trisetum alpestre*, melts at 220°, and has the specific rotation $[\alpha]_D = -44·47$. Irisin, $C_{96}H_{160}O_{80}$, from *Iris pseudo-acorus*, melts at 160°, and has the specific rotation $[\alpha]_D = -51·20$. Phleïn, from *Phleum pratense*, melts at 215°, and has the specific rotation $[\alpha]_D = -47·94$; the molecular weight could not be determined. J. W. L.

Animal Cellulose. By R. Schütze (*Chem. Centr.*, 1889, ii, 588; from *Mitt. pharm. Inst. Erlangen*, 2 *Heft*, 280—281).—The author has examined the mantle of *Phallusia mammillaris*, it being purified by boiling first with water, then repeatedly with 20 per cent. potassium hydroxide solution and 10 per cent. hydrochloric acid, and finally by digestion with hydrofluoric acid and hydrochloric acid.

The white cellulose substance contained 43·47 per cent. of carbon and 6·25 per cent. of hydrogen.

Solution of cupric oxide in ammonia dissolves the substance, and solution of iodine in zinc chloride or sulphuric acid stains it variously from red to violet. Nitric and sulphuric acids form an explosive nitrate with it, which is somewhat soluble in ether.

When heated with 10 per cent. sulphuric acid in a closed flask at 100°, a substance is formed which reduces Fehling's solution, and which ferments with yeast, with formation of carbonic anhydride.

The ether extract of the mantle contained small quantities of cholesterin, fat and free fatty acids, oleïc, valeric, and probably also palmitic and stearic acids.

The mineral matter included in the cuticle freed from fat consisted of: Silica 2·76, alumina 9·52, ferric oxide 15·81, phosphoric acid (combined with iron and aluminium) 12·72, calcium phosphate 3·91, calcium carbonate 49·22, and magnesium carbonate 6·03 per cent.

J. W. L.

Lignin. By G. LANGE (*Zeit. physiol. Chem.*, **14**, 217—226).—The investigation of the lignin of beech and ash wood previously recorded (Abstr., 1889, 1235) has in the present research been extended to that of pine wood (*Pinus abies*, L.). The lignin was prepared from this by the same methods as those previously employed; it was found to consist of 52 to 55 per cent. of cellulose, two brown substances called lignic acid; and as a result of fusing with alkali, formic, acetic, and traces of higher fatty acids, oxalic acid, catechol, protocatechuic acid, ammonia, and traces of higher bases were obtained. No succinic acid was obtained, as Erdmann stated (*Annalen*, **138**, 1). The percentage compositions of the lignic acids obtained from the three varieties of wood were as follows:—

	Lignic acid soluble in alcohol.		Insoluble in alcohol.	
Beech	C, 61·475;	H, 5·48	C, 59·04;	H, 5·37
Ash	„ 61·61	„ 5·47	„ 58·83	„ 5·15
Pine	„ 61·28	„ 4·95	„ 60·51	„ 5·22

Experiments designed to ascertain the constitution of these substances were unsuccessful.

W. D. H.

Gum Tragacanth. By J. OGLE (*Pharm. J. Trans.* [3], **20**, 3).—A sample of Syrian tragacanth yielded moisture 18·92, soluble gum 35·94, ash 2·75, and insoluble gum 42·39 per cent. The precipitate produced in the aqueous solution by the addition of alcohol was found not to be identical with arabin, and no evidence of the presence of starch could be obtained.

R. R.

Absence of Rotatory Power in Amine Salts. By J. A. LE BEL (*Bull. Soc. Chim.* [3], **2**, 305).—The order in which the substitution of radicles is effected in the NH_3 molecule does not influence the nature of the resulting amine, from which it follows that either the molecule alters its configuration according to the substitution, or that intramolecular migration of the substituted radicles occurs; if then in the former case the radicles are definitely located a compound of the formula $Cl{\cdot}NHR^1R^2R^3$ should exhibit rotatory power, since R^1, R^2, and R^3 cannot be in the same plane. With a view to determine this experimentally, the author prepared methylethylpropylamine hydrochloride, which he found to be devoid of rotatory power, and consequently the first hypothesis is untenable.

T. G. N.

Propargylamine and Derivatives of Allylamine. By C. PAAL and C. HERMANN (*Ber.*, **22**, 3076—3085).—*Dibromopropylamine hydrobromide*, $C_3H_5Br_2{\cdot}NH_2.HBr$, is obtained when an ice-cold, aqueous solution of allylamine is slightly acidified with concentrated hydrobromic acid, and then treated with bromine (1 mol.); the yield is

quantitative. It separates from hot water in well-defined, transparent crystals, melts at 164°, and is only sparingly soluble in hot alcohol and cold water, but readily in hot water; it is not decomposed by moderately concentrated sulphuric acid, even when boiled therewith for half an hour. The *salt* $(C_3H_5Br_2{\cdot}NH_2)_2,2HBr,PtCl_4$ crystallises in orange-red plates and decomposes at 200°, but without melting. The *salt* $C_3H_5Br_2{\cdot}NH_2,HBr,AuCl_3$ crystallises in dark-red needles, melts at 124°, and is moderately easily soluble in water.

Bromallylamine hydrobromide melts at 175° and not at 223—224°, as previously stated (compare Paal, Abstr., 1889, 117).

In preparing bromallylamine salts by the method previously described, it is better to neutralise the aqueous distillate containing the base with a dilute mineral acid, instead of collecting the distillate in excess of acid; in this way the formation of additive-componnds is avoided.

Tribromopropylamine hydrobromide, $C_3H_4Br_3{\cdot}NH_2,HBr$, prepared by treating bromallylamine hydrobromide with bromine in well-cooled, aqueous solution, crystallises from water in large, colourless plates containing water of crystallisation; the crystals effloresce on exposure to the air, and melt at 210° with partial decomposition. It crystallises from alcoholic ether in slender needles, and is moderately easily soluble in hot alcohol.

A *base*, $C_3H_5Br_2N$ or $(C_3H_5Br_2N)_2$, is formed when tribromopropylamine hydrobromide is treated with alcoholic potash; on distilling with steam, neutralising the distillate with hydrobromic acid, and concentrating the solution, the *hydrobromide*, $C_3H_5Br_2N,HBr$, is obtained in colourless crystals. This salt melts at 214°, does not combine with bromine, and is readily soluble in water, but only sparingly in alcohol. The *salt* $(C_3H_5Br_2N)_2.2HBr,PtCl_4$ crystallises in golden scales, and decomposes at 230°, but without melting. The salt $C_3H_5Br_2N,HBr,AuCl_3$ forms small, yellow, well-defined crystals. The free *base* is a yellowish, unstable oil; it does not give the carbylamine reaction, and it yields an oily nitrosamine which is insoluble in water and dilute mineral acids.

Propargylamine, $C_3H_3{\cdot}NH_2$, is formed when a dibromopropylamine salt is heated for $1\frac{1}{4}$ hours at 100° in a sealed tube with an alcoholic solution of sodium ethoxide (4 mols.). The contents of the tube are transferred to a flask and heated on the water-bath until most of the alcohol has distilled, the distillate being collected in an alcoholic solution of oxalic acid. The acid *oxalate*, $C_3H_3{\cdot}NH_2,C_2H_2O_4$, separates during the process in slender, colourless needles, which are perfectly pure if the above conditions are observed. It is only very sparingly soluble in boiling alcohol, but readily in water, from which it separates in large plates melting at 143°; its dilute aqueous solution gives a purple-red coloration with auric chloride. The yield of the oxalate is about 50 per cent. of the theoretical; the residue in the flask contains not inconsiderable quantities of a non-volatile base. All attempts to isolate propargylamine were unsuccessful; it seems to be much more readily soluble in water and concentrated alkalis than ammonia or methylamine. *Propargylamine silver* is precipitated when a solution of silver nitrate in excess of ammonia is added to an ammo-

niacal solution of the oxalate; it is a colourless compound, darkens gradually on exposure to the air, and explodes when heated. The *picrate*, $C_3H_3{\cdot}NH_2,C_6H_3N_3O_7$, prepared by precipitating an alcoholic solution of the base with picric acid, crystallises in large, reddish plates, melts at 189°, and is insoluble in ether. The *hydrochloride*, $C_3H_3{\cdot}NH_2,HCl$, prepared by passing hydrogen chloride into an alcoholic solution of the base, crystallises in colourless plates, is readily soluble in water and alcohol, and decomposes on exposure to light. The *hydrobromide*, $C_3H_3{\cdot}NH_2,HBr$, crystallises in thin, colourless plates, begins to soften at 130°, melts at 171°, and decomposes on exposure to light.

Methylpropargylamine hydriodide, $C_3H_3{\cdot}NHMe,HI$, is obtained when an alcoholic solution of propargylamine is treated with methyl iodide; it crystallises in long, colourless, very hygroscopic needles, melts at 83°, and decomposes on exposure to light. The free *base* is a yellowish, volatile oil, of ammoniacal odour. The *oxalate*, $C_4H_7N,C_2H_2O_4$, crystallises from dilute alcohol in colourless needles melting at 141°.

Ethylpropargylamine hydriodide crystallises in long needles; *propylpropargylamine hydrobromide* crystallises in plates melting at 180°.

Isoamylpropargylamine is formed when isoamyldibromopropylamine hydrobromide is treated with sodium ethoxide, as described above; the contents of the tube are treated with a little water to dissolve the sodium bromide, the solution saturated with potassium carbonate, the supernatant alcohol separated, dried over potash and distilled, the distillate being collected in an alcoholic solution of oxalic acid. The *oxalate*, $C_3H_3{\cdot}NH{\cdot}C_5H_{11},C_2H_2O_4$, is thus obtained in small, colourless needles melting at 204°; it crystallises from water with 1 mol. H_2O. The free *base* is liquid. The *hydrobromide*, $C_8H_{15}N,HBr$, crystallises in nacreous plates melting at 186°. F. S. K.

Action of Heat on Chloral-ammonia. By A. Béhal and Choay (*Compt. rend.*, **109**, 817—820).—Personne showed that when chloral-ammonia is heated at 100° it yields chloroform and formamide, but the decomposition is not complete. If chloral-ammonia is heated in a retort at 100° until chloroform ceases to distil over, a black viscous mass with a slightly alliaceous odour is left; this contains ammonium chloride, formamide, and some other compounds.

If this residue is boiled with strong alcohol, the latter on cooling deposits crystals of the chloralimide described by Pinner and Fuchs, the yield being about 5 per cent. of the original chloral-ammonia. Chloralimide forms long, colourless, tasteless needles slightly soluble in water, more soluble in alcohol, very soluble in ether. It is decomposed by a cold aqueous solution of platinic chloride with formation of chloral and ammonium platinochloride. It is not affected by water in sealed tubes at 150°, but at 170° decomposes completely into chloroform and formamide, which undergo partial decomposition and yield some ammonium chloride, carbonic anhydride, and hydrochloric and formic acids. Chloralimide in doses of 0·25 to 0·50 gram has remarkable antipyretic and analgesic properties.

If the residue in the retort, either before or after extraction with

alcohol, is boiled with a large quantity of water, the liquid deposits crystals on cooling, and if these are purified by treatment with animal charcoal and recrystallisation from alcohol, the compound $C_4Cl_3H_5N_2O_2$ is obtained in long, colourless, tasteless, inodorous prisms, very slightly soluble even in boiling water, more soluble in alcohol, especially if heated, and very soluble in ether. It melts at 216—217°, and almost immediately decomposes with evolution of gas. It is partially decomposed by platinic chloride, and when heated with excess of acetic anhydride it yields an acetyl-derivative of the composition $C_4Cl_3H_4AcN_2O_2$, which crystallises in long needles very soluble in acetic acid, almost insoluble in water, and only slightly soluble in alcohol or benzene. This derivative is not affected by a neutral or acid alcoholic solution of platinic chloride; it is stable even at a high temperature, but does not melt without decomposing.

The first componnd, $C_4Cl_3H_5N_2O_2$, is probably didehydrotrichlorodihydroxypiperazine, formed by the condensation of 2 mols. of chloral-ammonia with elimination of 3 mols. of hydrogen chloride, but this view requires further investigation. C. H. B.

The Indian Grass Oils. By F. D. DODGE (*Amer. Chem. J.*, **11**, 456—469).—These are at least five in number, namely, oils of citronella, lemon-grass, Indian or Turkish geranium, ginger-grass, and vetivert or cus-cus. They are derived from various tropical grasses of the genus *Andropogon*, but there is some confusion as to the particular species from which the individual oils are obtained.

Citronella Oil. The commercial varieties are often adulterated with kerosene; the pure oil is a clear, greenish-yellow liquid with a sharp burning taste and a strong aromatic odour. Its sp. gr. at 16° is 0·8770, at 26·5° 0·8750. It distils between 200° and 240°, leaving 10 per cent. of a thick oily residue, having a pungent odour. It gives most of the reactions of aldehydes, combining with hydrogen sulphites and with phenylhydrazine, although not with ammonia; it also reacts with acetic and benzoic chlorides, and gives a mirror with an ammoniacal silver solution. Two litres of the oil were distilled in a current of steam, and collected in fractions of 1100 c.c. and 400 c.c., the residue of 500 c.c. not being readily volatile. The first fraction (1100 c.c.) was treated with a solution of sodium hydrogen sulphite, the mixture being kept cool with ice and water. The liquid solidified to a white magma, and the sodium hydrogen sulphite compound was then pressed between flannel and washed with ether; the filtrate yielded 350 c.c. of residual oil. The sodium hydrogen sulphite compound was mixed with dry sodium carbonate and distilled in a current of steam; about 700 c.c. of aldehyde was thus obtained. This was shown by analyses, and a vapour-density determination, to have the formula $C_{10}H_{16}O$, and is thus isomeric with borneol and geraniol. The author names it *citronellic aldehyde*, and considers it to be β-methyl-δ-isobutylallylacetaldehyde, $CH_2Pr^{\beta}·CH\!:\!CHMe·CH_2·CHO$, since this formula is most in accordance with its reactions. It unites with 2 atoms of bromine, and when reduced with sodium amalgam and acetic acid it yields *citronellyl alcohol*, $C_{10}H_{20}O$, boiling at 225—230°; this decolorises bromine solution, and has a pleasant

odour of roses. It forms compounds with phenylhydrazine, with aniline and paratoluidine, and with acetic acid, but these products have not yet been isolated. It is dextrorotatory, and when oxidised, appears to yield fatty acids; with potassium permanganate, it yields a mixture of acids smelling strongly of ordinary valeric acid. When treated with phosphoric anhydride, some large, colourless plates (melting at 140°) were deposited, and two oils formed, one boiling at 175°, which was shown by analysis to be an impure terpene, and one boiling above 300°, which had a pleasant odour resembling the high-boiling fractions of citronella oil.

The 350 c.c. filtered from the sodium hydrogen sulphite compounds yielded (1.) 75 c.c of a light oil, boiling at 177°, and having a pleasant, citrene-like odour; this was analysed, and its vapour-density determined, the results indicating that it was an impure terpene; (2.) 120 c.c. of a thicker oil, of rose-like odour, boiling at 222—224°, and of sp. gr. = 0·8741 at 26·5°, which appeared to be citronellyl alcohol; (3.) 100 c.c. boiling above 240°, dark brown, viscid, and having a peculiar odour.

The residual 500 c.c. of the original oil not readily volatile in steam was treated with sodium hydrogen sulphite, and yielded about 10 c.c. of citronellic aldehyde, and a residual 475 c.c., which when distilled behaved like the residue from the other sulphite precipitate, but yields a much larger amount of high-boiling products, which oxidise readily, and are difficult to treat. Citronella oil therefore contains citronellic aldehyde and alcohol, together with a terpene and oils boiling above 240°. The study of these oils is to be continued. C. F. B.

Derivatives of Tetrachlorodiacetyl and of Tetrachloracetone. By S. Levy, F. C. Witte and A. Curchod (*Annalen*, **254**, 83—114; compare Abstr., 1889, 1160 and 1136).—The compound, $C_{16}H_{14}Cl_2N_4O$, prepared by boiling tetrachlorodiacetyl (Abstr., 1889, 390) with excess of phenylhydrazine in alcoholic solution, combines with phenylhydrazine when warmed therewith, with evolution of ammonia; it is decomposed by alcoholic potash with liberation of aniline, and when treated with fuming nitric acid in sulphuric acid solution, it is converted into a yellow compound, which is precipitated on adding water.

Tetrachlorodimethylquinoxaline, $C_6H_4<\begin{matrix}N:C\cdot CHCl_2\\ |\\ N:C\cdot CHCl_2\end{matrix}$, separates in crystals when tetrachlorodiacetyl (1 mol.) is treated with orthophenylenediamine (1 mol.) in hot aqueous solution. It crystallises from alcohol in small, colourless, nacreous plates, and from benzene in large, well-defined, triclinic plates, $a : b : c = 0·8198 : 1 : 0·9698$; $\alpha = 92° 4'$, $\beta = 121° 56'$, $\gamma = 85° 22'$; it melts at 177°, and distils at a high temperature with partial decomposition. It is readily soluble in hot chloroform, alcohol, and benzene, but only sparingly in the cold solvents and in ether, and is insoluble in water; it dissolves in concentrated sulphuric acid with a yellow coloration

The compound $C_2H_4(NH\cdot CHCl\cdot CO\cdot CO\cdot CHCl_2)_2$ can be obtained by gradually adding an aqueous solution of tetrachlorodiacetyl to an ice-cold aqueous solution of ethylenediamine, but it is best prepared by dissolving the two substances in 95 per cent. alcohol,

and warming until the colour of the solution changes to red. It crystallises from dilute alcohol in colourless, slender needles, melts at 222—223° with decomposition, and is readily soluble in alcohol, ether, chloroform, and benzene, but only sparingly in light petroleum, and almost insoluble in water.

Trichloramidodiacetyl, $CHCl_2·CO·CO·CHCl·NH_2$, prepared by gradually adding ammonia (3—4 c.c.) to a dilute alcoholic solution of tetrachlorodiacetyl (2 grams) and heating the mixture to boiling, crystallises from benzene in colourless needles, melts at 127°, and is readily soluble in alcohol and ether, but only moderately in water or benzene and very sparingly in light petroleum. It has feeble basic properties, and is decomposed by soda with evolution of ammonia. When treated with hydrochloric acid, it is converted into two substances, one of which crystallises in large prisms melting at 157°, the other in small, colourless needles of lower melting point.

Tetrachlorodiacetyldicyanhydrin,

$$CHCl_2·C(OH)(CN)·C(OH)(CN)·CHCl_2,$$

is formed when tetrachlorodiacetyl is heated with excess of concentrated hydrocyanic acid at 30—40° for 4 to 5 hours. The product is extracted with ether, and repeatedly treated with light petroleum to free it from the monocyanhydrin. It separates from a mixture of ether and light petroleum in spherical aggregates, sinters together at about 110°, and melts at about 135—137° with decomposition. It is readily soluble in water, ether, and alcohol, but only sparingly in carbon bisulphide, chloroform, and benzene, and insoluble in light petroleum. It is decomposed when warmed with water at a temperature below 100°. The *diacetyl*-derivative, $C_{10}H_8Cl_4N_2O_4$, prepared by heating the cyanhydrin with acetic chloride, crystallises from dilute alcohol in colourless needles, melts at 163°, decomposes at a higher temperature, and is readily soluble in ether, alcohol, and chloroform, but only sparingly in benzene and boiling water, and insoluble in light petroleum.

The *monocyanhydrin*, $CHCl_2·C(OH)(CN)·CO·CHCl_2$ (see above), crystallises from benzene, in which it is readily soluble, in colourless plates, melts at 110—111°, and decomposes at about 155°.

Tetrachlorodimethyltartarimide, $NH<\begin{matrix}CO·C(OH)·CHCl_2 \\ | \\ CO·C(OH)·CHCl_2\end{matrix}$, is obtained, together with a small quantity of a yellowish acid, when the dicyanhydrin (2 grams) is heated at 110° for two hours with 35 per cent. hydrochloric acid (15 c.c.). It separates from a mixture of benzene and ether in dendritic crusts, melts at 239—240°, and is readily soluble in alcohol, ether, and hot water, but almost insoluble in chloroform, benzene, and light petroleum. The *triacetyl*-derivative, $C_{12}H_{11}Cl_4NO_7$, crystallises from dilute alcohol in small, colourless prisms or needles, melts at 176—177° with decomposition, and is readily soluble in alcohol and ether, but only sparingly in hot, and insoluble in cold water.

Tetrachlorodimethyltartaramide,

$$CHCl_2·C(OH)(CONH_2)·C(OH)(CONH_2)·CHCl_2,$$

is formed when concentrated sulphuric acid is gradually added to a concentrated glacial acetic acid solution of the dicyanhydrin, and the mixture warmed gently until the crystals which separate from the solution have redissolved. It crystallises from boiling chloroform in slender, colourless needles, melts at 183°, and is readily soluble in water, alcohol, and ether, but only very sparingly in boiling chloroform, and insoluble in light petroleum. It is converted into the imide by 35 per cent. hydrochloric acid at 110°, or when warmed with sulphuric acid in glacial acetic acid solution.

Tetrachlorhydroxyisobutyramide (m. p. 156°) is best prepared from tetrachloracetonecyanhydrin (Abstr., 1889, 1136), by dissolving the latter in glacial acetic acid, adding concentrated sulphuric acid, and heating to boiling for a few minutes. It crystallises from ether in four-sided pyramids, is readily soluble in alcohol and moderately easily in benzene, but only sparingly in chloroform and insoluble in light petroleum.

The compound $C_4H_4Cl_3NO_2$, probably the amide of trichloropropyleneoxidecarboxylic acid, is obtained when the preceding compound is treated with sodium carbonate in the cold. It crystallises in needles, melts at 127°, and is readily soluble in ether, alcohol, chloroform, and benzene, moderately easily in carbon bisulphide, and sparingly in light petroleum.

Tetrachlorhydroxyisobutyric acid, $OH·C(CHCl_2)_2·COOH$, prepared by heating the amide at 110—120° with hydrochloric acid of sp. gr. 1·16, crystallises from light petroleum in needles, melts at 69—71°, and is readily soluble in water, ether, alcohol, chloroform, and benzene, but only sparingly in carbon bisulphide and light petroleum. The *potassium* salt, $C_4H_3Cl_4O_3K$, crystallises from water in transparent prisms, and is very readily soluble in water, but only sparingly in alcohol; it is decomposed by hot water. F. S. K.

Preparation of Acetic Chloride and Chloracetic Acid. By V. Auger and A. Béhal (*Bull. Soc. Chim.* [3], **2**, 144—145).—To prepare acetic chloride, sulphur (1 mol.) or sulphur dichloride (1 mol.) is placed in a flask with glacial acetic acid (2 mols.), and chlorine is passed into the mixture cooled by ice and salt, until no further absorption occurs; after distillation of the resulting product at 60°, and agitation of the distillate with mercury or powdered copper to remove a sulphur compound, subsequent fractionation yields a pure product; 600 grams of acetic acid gave 500 grams of acetic chloride.

Chloracetic acid is obtained under conditions similar to those above, except that the mixture of sulphur and acetic acid is to be boiled: chloracetic acid is obtained in a very pure condition, only traces of acetic chloride and of acetic anhydride being produced; 800 grams of acetic acid yielded, after 12 hours' chlorination, 1000 grams of the monochlorinated derivative. T. G. N.

Action of Triethylamine on Ethyl α-Bromobutyrate, and Ethyl α-Bromopropionate. By M. E. Duvillier (*Bull. Soc. Chim.* [3], **2**, 139—142; compare Abstr., 1888, 249).—The action of tri-

ethylamine (3 mols.) on ethyl α-bromobutyrate (1 mol.) at 100° yielded a considerable amount of α-hydroxybutyric acid, and this was accompanied by a small quantity of butyric and crotonic acids, whilst traces of tetrethylammonium hydroxide were produced.

The substitution of ethyl α-bromopropionate for ethyl α-bromobutyrate determines the production of much lactic acid and of small quantities of tetrethylammonium hydroxide, and of betaïne (1 per cent.), in which latter respect the bromo-derivative differs from the corresponding chloro-compound, from which, under similar conditions, Brühl could not obtain betaïne (this Journal, 1876, i, 699).

T. G. N.

Preparation of Alkyl Salts of β-Ketonic Acids. By J. HAMONET (*Bull. Soc. Chim.* [3], **2**, 334—337; compare Abstr., 1888, 235).—The product of the action on a normal acid chloride (1 mol.) of sublimed ferric chloride (2 mols.) is poured into cold absolute alcohol, and when the reaction is completed the upper layer of liquid, which contains the salt of the β-ketonic acid, is dried and fractionated.

Propionic chloride yields by this process ethyl α-propiopropionate, a colourless liquid of sp. gr. 0·9987 at 0°, boiling at 196—197°.

Butyric chloride and heptoic chloride, when similarly treated, yield respectively *ethyl α-butyrobutyrate*, boiling at 217—219°, and *ethyl α-heptoheptoate*, boiling at 290—292°.

As ethyl α-butyrobutyrate, when treated by Ceresole's method, yields butyrobutyric acid, whose barium salt decomposes on warming into a carbonate and butyrone, it is to be regarded as a β-ketonate.

Isobutyric acid yielded, by the author's method, valerone and *ethyl valerovalerate*, boiling at 232—234°, and of sp. gr. 0·9492 at 0°.

From a mixture of propionic and butyric chlorides the author obtained, by this method, ethyl propyl ketone, boiling at 122°, and *ethyl α-propiobutyrate*, boiling at 207—209°, and of sp. gr. 0·9884 at 0°.

The theory of the reactions is discussed. T. G. N.

Ethylenelactic Acid from Flesh Extract. By E. KLIMENKO (*Ber.*, **22**, 3182—3183).—The author corrects the statement of Siegfried (*Ber.*, **22**, 2711) that he (Klimenko) was unable to isolate an amorphous zinc salt from lactic acid obtained from flesh extract.

F. S. K.

Alkyl Hydrogen Oxalates, Dichloroglycollates, and Chloroxalates: Tetralkyl Oxalates. By R. ANSCHÜTZ (*Annalen*, **254**, 1—42; compare Abstr., 1886, 785 and 1011).—The alkyl hydrogen oxalates gradually undergo spontaneous decomposition into the neutral salt and oxalic acid; they decompose potassium acetate in alcoholic solution, forming alkyl potassium oxalates.

Methyl phenyloxamate, NHPh·CO·COOMe, prepared by heating methyl oxalate with aniline, crystallises from alcohol, in which it is readily soluble, in large, yellowish plates, and from light petroleum in small, colourless needles, melting at 114°. The corresponding *propyl* salt, NHPh·CO·COOPr, crystallises from alcohol in colourless

needles, melts at 92°, and is readily soluble in alcohol, but only sparingly in light petroleum. The *isopropyl* salt crystallises from light petroleum in long, white, silky needles and melts at 52°. The *isobutyl* salt forms small, colourless plates, melts at 85°, and is readily soluble in alcohol. The *amyl* salt crystallises from light petroleum in needles, and melts at 50°.

Dimethyl dichloroglycollate, $OMe\cdot CCl_2\cdot COOMe$, prepared by heating methyl oxalate with phosphoric chloride for 12 to 18 hours at 130—135°, and fractionating the crude product under reduced pressure, is a colourless liquid boiling at 179—181° (at 72°, about 12 mm.).

Diisobutyl dichloroglycollate, $C_4H_7\cdot O\cdot CCl_2\cdot COOC_4H_7$, is a colourless liquid boiling at 128° (about 14 mm.).

The alkyl chloroxalates can be obtained by distilling the dialkyl dichloroglycollates under the ordinary pressure.

Methyl chloroxalate, $COCl\cdot COMe$, is best prepared by heating dimethyl dichloroglycollate at 200—215° for 40 hours; it is a colourless liquid boiling at 118—120°.

The corresponding *ethyl* salt, $COCl\cdot COEt$, boils at 135—136° (at 30°, about 10 mm.), the normal *propyl* salt at 153—154° (at 50°, about 12 mm.), the *isobutyl* salt at 163—165° (at 52°, about 10 mm.), and the *amyl* salt at 183—185° (at 68°, about 10 mm.).

Tetralkyl-derivatives of oxalic acid can be obtained by treating the dialkyl dichloroglycollates with sodium compounds of alcohols in alcoholic ethereal solution.

Tetramethyl oxalate, $C(OMe)_3\cdot COOMe$, is a colourless liquid boiling at 75—76° (about 12 mm.). The corresponding *ethyl* salt, $C(OEt)_3\cdot COOEt$, boils at 98° (about 12 mm.), the normal *propyl* salt at 256—257° (at 129—130°, about 12 mm.), the *isobutyl* salt at 146° (about 10 mm.), and the *amyl* salt at 190° (about 10 mm.).

Dimethyl diethyl oxalate, $OMe\cdot C(OEt)_2\cdot COOMe$, is formed when dimethyl dichloroglycollate is treated with sodium ethoxide in ethereal solution; it boils at 90—92° (about 13 mm.). If the reaction is carried out in alcoholic ethereal solution, a liquid boiling at 94·5—96·5° (about 12 mm.), probably methyl triethyl oxalate, is obtained.

When dimethyl dichloroglycollate is heated with oxalic acid at about 50°, carbonic oxide, carbonic anhydride, and hydrogen chloride are evolved, and the residue consists of methyl oxalate; other dialkyl dichloroglycollates could probably be converted into the corresponding alkyl oxalate in like manner.

When tetramethyl oxalate is treated with phosphoric chloride, it is converted into methyl oxalate with evolution of methyl chloride; tetrethyl oxalate yields ethyl oxalate under the same conditions.

F. S. K.

Constitution of Succinic Chloride. By W. O. Emery (*Ber.*, **22**, 3184—3186).—Methyl succinate, prepared by treating succinic chloride with sodium methoxide in ethereal solution, is identical with the compound obtained by heating silver succinate with methyl iodide at 100°; it melts at 19° and boils at 80° (10—11 mm.).

F. S. K.

Substituted Succinic Acids. By C. A. BISCHOFF (*Ber.*, 22, 3179—3180).—The author has hydrolysed a number of ethereal salts of alkyl- and benzyl-isobutenyltricarboxylic acids; two isomeric acids were obtained in every case. A large number of ethereal salts of other unsaturated tricarboxylic acids will be examined in this direction. F. S. K.

Synthesis of Aconitic Acid from Acetylenedicarboxylic Acid. By J. M. LOVÉN (*Ber.*, 22, 3053—3056).—When dibromosuccinic acid is boiled for a long time with a slight excess of alcoholic potash, it is converted into oxalic and aconitic acids.

Acetylenedicarboxylic acid, under the same conditions, gives the same products, so that the bromosuccinic acid is first converted into acetylenedicarboxylic acid; the yield of aconitic acid is 30 per cent. or more of the acetylenedicarboxylic acid employed. F. S. K.

Oxidation of Ketones by Potassium Permanganate in Alkaline Solution. By G. GLÜCKSMANN (*Monatsh.*, 10, 770—782).—Potassium permanganate has no action on pinacoline in cold or warm neutral solution; but when the ketone (20 parts), suspended in water, is gradually treated with a mixture of potassium permanganate (63 parts) and sodium hydroxide (20 parts), dissolved in water (2 litres), oxidation takes place, the products being the until now unknown *trimethylpyruvic acid*, $C_6H_{10}O_3$, and a little trimethylacetic acid. The new acid crystallises in colourless, irregular-pointed prisms, having a peculiar acid odour, is sparingly soluble in cold, but readily soluble in hot water and in ether, is fairly soluble in benzene, carbon bisulphide, chloroform, and carbon tetrachloride, is volatile in a current of steam, melts at 90—91°, and has the constitution $CMe_3 \cdot CO \cdot COOH$.

With phenylhydrazine, trimethylpyruvic acid forms a compound $C_{12}H_{16}N_2O_2$, which crystallises from dilute alcohol in long, pale-yellow needles, and melts at 157—158° with evolution of carbonic anhydride and formation of aniline. On heating with a 20 per cent. solution of hydrochloric acid, trimethylpyruvic acid is not regenerated, but an aldehyde, probably that of trimethylacetic acid, is the product. The calcium salt of trimethylpyruvic acid, $(C_6H_9O_3)_2Ca + 3H_2O$, is very soluble in water; the sodium salt is anhydrous, and crystallises in long, colourless, rhombic plates; the silver salt, which is also anhydrous, in gleaming scales.

Trimethylpyruvic acid is converted into trimethylacetic acid when oxidised with silver oxide or with potassium dichromate and sulphuric acid. On reduction with eight times its weight of 4 per cent. sodium amalgam it is converted into *trimethylethylidenelactic acid*, $CMe_3 \cdot CH(OH) \cdot COOH$, in nearly theoretical quantity. This acid forms colourless, probably monosymmetric crystals ($a : b : c =$ 1·45 : 1 : 1·10, approx.), melts at 87—88°, is readily soluble in water and in ether, and gives copper, silver, and zinc salts, which are not very characteristic.

The oxidation of pinacoline to trimethylpyruvic acid is not in

accordance with Popow's rule for the oxidation of ketones, and the author, to explain the reaction, supposes that in the operation an intermediate condensation-product, $CMe_3 \cdot CO \cdot CH{:}CMe \cdot CMe_3$, is formed with elimination of 1 mol. of water, and that this condensation-product, on oxidation with 3 atoms of oxygen, is converted into trimethylpyruvic acid and pinacoline, the latter again undergoing the condensation and oxidation processes. The author has also succeeded in obtaining pyruvic acid by the oxidation of acetone with permanganate in alkaline solution, and suggests that the formation of trimethylpyruvic acid from pinacoline may perhaps be a typical reaction. G. T. M.

Isomeride of Tricarballylic Acid. By E. GUINOCHET (*Compt. rend.*, **109**, 906—908).—The action of sodium amalgam on the tribromotricarballylic acid formed by the action of bromine on aconitic acid yields an isomeride of tricarballylic acid. It crystallises in confused, almost opaque, macled prisms, and melts at 181°; carballylic acid melts at 158°, and crystallises in large, perfectly transparent prisms. It is only slightly soluble in water, whilst carballylic acid is very soluble. Its barium salt is crystallisable, anhydrous, and somewhat soluble in water; the calcium salt crystallises, with 12 mols. H_2O, in long, hard, transparent, efflorescent prisms. C. H. B.

Fucusol. By K. BIELER and B. TOLLENS (*Ber.*, **22**, 3062—3063). —A claim for priority. (Compare Maquenne, this vol., p. 33.)

Constitution of the Aromatic Nucleus. By S. A. SWORN (*Phil. Mag.* [5], **28**, 402—415, and 443—451).—Arguments are brought forward in favour of Thomsen's octahedral formula for benzene (Abstr., 1887, 362), these being chiefly based on the evidence of direct linkage between symmetrically disposed carbon-atoms (para-linkage). In some cases arguments derived from the study of pyridine-derivatives are applied by analogy to the derivatives of benzene, the author considering that this is justified by the result of recent researches. It is first shown that the central nucleus of anthracene is truly aromatic, and that in this nucleus the carbon-atoms are directly linked to one another. The abnormally low molecular volume and absorption of ultra-violet rays by anthracene, the oxidation of anthracene to a substance of the quinone type, and the oxidation of acridine to a quinoline-derivative, are all advanced in favour of the above views. The diketonic nature of quinone and its behaviour on reduction are best explained on the assumption of a para-linkage, the author being of opinion that when a para-linkage is broken the nucleus opens out into a hexagonal ring, and the remaining para-linkages are severed with the formation of olefinic bonds, this view being supported by Baeyer's work on the additive compounds of terephthalic acid. The formulæ of Meyer and Ladenburg represent benzene as containing para-linkages, but the optically active conine would have no asymmetric carbon-atom in the symbol derived from these formulæ, a requirement which is, however, satisfied by that of Thomsen. In the same way, symbols for naphthalene and fluorene

cannot be satisfactorily derived from the formulæ of Meyer and Ladenburg, but can be readily deduced from the Thomsen formula.

An objection to the Thomsen formula, which the author himself raises, is that were the configuration of the benzene-molecule as a whole octahedral, we should expect the crystals of benzene to belong to the regular system, whereas they are rhombic. It is considered, therefore, that the above formula requires still further development before it can be brought into accordance with all the facts.

H. C.

Paracyanobenzyl Chloride and its Derivatives. By W. Mellinghoff (*Ber.*, **22**, 3207—3217).—*Paracyanobenzyl chloride*, $CN\cdot C_6H_4\cdot CH_2Cl$, is obtained in a similar manner to orthocyanobenzyl chloride (Gabriel and Otto, Abstr., 1887, 1035), by passing chlorine into paracyanotoluene nearly at its boiling point, until the weight has increased 30 per cent., allowing to cool, and recrystallising the solid portion from alcohol. It forms colourless, well-developed, rhombic prisms, $a : b : c = 0{\cdot}7495 : 1 : 0{\cdot}4314$, melts at 79·5°, boils at 263° (uncorr.), and is sparingly soluble in hot water, more easily in alcohol, ether, chloroform, and benzene.

Paracyanobenzyl cyanide, $CN\cdot C_6H_4\cdot CH_2\cdot CN$, is formed when the above compound is treated with potassium cyanide. It crystallises from alcohol in needles, melts at 100°, boils above 360°, and is slightly soluble in hot water, more readily in alcohol, ether, and chloroform. It is the dinitrile of homoterephthalic acid, into which it may be converted in the manner shown below. There are seven possible intermediate products, all of which have been prepared.

Paracyanophenylacetamide, $CN\cdot C_6H_4\cdot CH_2\cdot CONH_2$, is prepared by warming the dry powdered dinitrile with 38 per cent. hydrochloric acid (15 parts) until effervescence commences. It separates from dilute alcohol in crystals which melt at 196·5 (uncorr.), and is soluble in hot water and alcohol. In addition to this compound, paracyanophenylacetic acid and a substance of unknown constitution, $C_{17}H_{11}N_3$, are also formed.

ω-Chloroparatoluamide, $CONH_2\cdot C_6H_4\cdot CH_2Cl$, is obtained by allowing paracyanobenzyl chloride to remain with concentrated sulphuric acid in the cold for 12 hours. It is a white, crystalline precipitate, melts at 173° (uncorr.), and is soluble in the common solvents.

ω-Cyanoparatoluamide, $CONH_2\cdot C_6H_4\cdot CH_2\cdot CN$, is formed by heating the foregoing compound with potassium cyanide. It crystallises from alcohol in small, colourless plates, melts at 182° (uncorr.), and is readily distinguished from the isomeric paracyanophenylacetamide by its appearance.

Paracyanophenylacetic acid, $CN\cdot C_6H_4\cdot CH_2\cdot COOH$, is prepared by heating paracyanobenzyl cyanide with fuming hydrochloric acid until the temperature has reached 105°, and then almost neutralising with ammonia. It forms prismatic crystals melting at 152° (uncorr.), and forms an emerald-green copper salt.

ω-Chloroparatoluic acid, $COOH\cdot C_6H_4\cdot CH_2Cl$, is formed when ω-chloroparatoluamide is heated with 25 times its weight of officinal hydrochloric acid for $1\frac{1}{4}$ hours. It crystallises from alcohol in microscopic

needles, melts at 199° (uncorr.), and yields a light-brown precipitate with solutions of copper salts.

ω-Cyanoparatoluic acid, $COOH\cdot C_6H_4\cdot CH_2\cdot CN$, is formed from the compound just described by acting on its potassium salt with potassium cyanide. It melts at 201° (uncorr.), and is readily soluble in hot water, alcohol, and ether, less so in cold water.

Homoterephthalamide, $CONH_2\cdot C_6H_4\cdot CH_2\cdot CONH_2$.—To prepare this substance, paracyanobenzyl cyanide is dissolved in 8 parts of cold concentrated sulphuric acid, and allowed to remain for 12 hours; water is then added, and the acid neutralised with ammonia. The amide forms a white precipitate or nodules of crystals, and melts at 235° (uncorr.). It is very sparingly soluble in indifferent solvents, but dissolves readily in concentrated hydrochloric acid.

Homoterephthalamic acid, $COOH\cdot C_6H_4\cdot CH_2\cdot CONH_2$, is obtained from ω-cyanoparatoluic acid by the action of cold concentrated sulphuric acid, and may be purified by crystallisation from alcohol, in which it is sparingly soluble. It melts at 261° (uncorr.), and forms a light-blue copper salt.

Homoterephthalisoamic acid, $CONH_2\cdot C_6H_4CH_2\cdot COOH$, is formed in like manner to the foregoing from paracyanophenylacetic acid. It melts at 229° (uncorr.), and is distinguished from its isomeride by greater solubility in alcohol, and by forming a malachite-green copper salt.

Homoterephthalic acid, $COOH\cdot C_6H_4\cdot CH_2\cdot COOH$, is best obtained from the diamide by heating it for 3—4 hours with 20 parts of 25 per cent. hydrochloric acid, and crystallising the product from dilute alcohol. It dissolves in 7 parts of alcohol at 30°, and in 100 parts of water at 50°, but is almost insoluble in ether and benzene. It melts at 285—288° (uncorr.), and gives with copper salts a verdigris-like precipitate.

The compounds described as homoterephthalic acid by Paternò (*Gazzetta*, **7**, 361), and as insolinic acid by Hofmann (*Annalen*, **97**, 177), probably consist of impure terephthalic acid. H. G. C.

Chloranisoïls. By L. Hugounenq (*Bull. Soc. Chim.* [3], **2**, 273—280).—Chlorine is passed into cold anisoïl (432 grams), in the dark, until the weight increases to 680 grams; after washing and subsequent steam distillation, the portion which fractionates at 230—237·5° is retained. This liquid resisted crystallisation, and not until it had been exposed to the cold of a winter's night were acicular crystals obtained, which, after removal of the trichlorinated derivative by pressure, were recrystallised from alcohol. As thus obtained, dichloranisoïl melts at 27—28°, but the presence of traces of trichloranisoïl reduces the melting point to 16°. From the alcoholic mother liquor, large, orthorhombic prisms of *dichloranisoïl* separate, having the axial ratios $a : b : c = 0·6556 : 1 : 0·5231$. The substance boils at 232—233° under a pressure of 743·45 mm. (corr.); it is soluble in alcohol, ether, benzene, and chloroform, but is insoluble in water. When heated at 145° in sealed tubes with hydriodic acid (sp. gr. 1·7), methyl iodide and dichlorophenol (1 : 2 : 4) were obtained.

Dichloronitroanisoïl is obtained by the action of fuming nitric acid

on dichloranisoïl; it crystallises from alcohol in pale, yellowish-green needles, melting at 43·5°.

Trichloranisoïl is formed by passing chlorine into cold anisoïl until the hydrogen chloride evolved and absorbed by cold water equals the weight of anisoïl employed; the product is washed, dissolved in boiling alcohol, and recrystallised, when needles are obtained which melt at 60·5°, are soluble in benzene, chloroform, and carbon bisulphide, and distil at 240° under a pressure of 738·2 mm. (corr.). When heated at 180° in sealed tubes with concentrated hydrochloric acid, or at 140—150° with hydriodic acid, trichlorophenol [1 : 2 : 4 : 6] is produced.

Trichloronitroanisoïl [OMe : Cl_3 : NO_2 = 1 : 2 : 4 : 6 : 3], forming long, nacreous needles melting at 48—50°, results from the action of a mixture of sulphuric and fuming nitric acids on the preceding derivative. A *trichlorodinitroanisoïl* [1 : 2 : 4 : 6 : 3 : 5], crystallising in prisms which melt at 90—91°, is formed by the action of nitric and sulphuric acids on trichloroanisoïl at 70—75°.

Tetrachloranisoïl results from the action of chlorine at 70° on anisoïl containing 5 to 6 per cent. of iodine; some pentachloranisoïl is also produced, and may be separated by recrystallisation from hot alcohol. Tetrachloranisoïl crystallises in slender needles, which are soluble in alcohol, ether, chloroform, benzene, and carbon bisulphide; it is sublimable, and boils with partial decomposition at 278° under a pressure of 745·85 mm. (corr.). When hydrolysed by hydrochloric acid at 175°, or by hydriodic acid at 150°, orthotetrachlorophenol, hitherto undescribed, is produced; this substance the author is studying.

Pentachloranisoïl crystallises in long, hard crystals, melts at 107—108°, and is slightly soluble in cold alcohol, easily in benzene, carbon bisulphide, chloroform, and boiling alcohol. Under a pressure of 745·45 mm., it boils at 289° with partial decomposition. When heated with hydriodic acid at 186°, it yields pentachlorophenol.

T. G. N.

Derivatives of Symmetrical Dinitroresorcinol. By F. KEHRMANN (*J. pr. Chem.* [2], **40**, 494—497).—*Chlorodinitroresorcinol* [$(OH)_2$: Cl : $(NO_2)_2$ = 1 : 3 : 2 : 4 : 6] is obtained by suspending finely powdered dinitroresorcinol in ether, and passing chlorine, diluted with carbonic anhydride, through the liquid. It forms long, yellow, vitreous prisms melting at 181—182°, and soluble in most solvents. The *neutral potassium salt* was obtained.

The *chlorodiamidoresorcinol stannochloride* is obtained by reducing the nitro-compound with excess of stannous chloride, but attempts to isolate the hydrochloride or base result in the formation of *chloramidohydroxyquinoneimide* [O : Cl : OH : NH : NH_2 = 1 : 2 : 3 : 4 : 6], which is best obtained by treating the stannochloride with ferric chloride in aqueous solution; it crystallises in violet needles, and is converted into chlorodihydroxyquinone (next abstract) by dilute potash solution.

A. G. B.

Derivatives of Metadichloroquinone. By F. KEHRMANN and W. TIESLER (*J. pr. Chem.* [2], **40**, 480—494).—Metadichloroquinone

is best prepared as follows :—Commercial trichlorophenol (200 grams) is dissolved in sufficient glacial acetic acid at 40—50°, and is mixed with a solution of chromic anhydride (120 grams) in sufficient water to dissolve it and twice that volume of glacial acetic acid. After the mixture has remained at 30—40° for a quarter of an hour, much water is added; this precipitates the metadichloroquinone in yellow needles; it melts at 121°. *Metadichloroquinol*, $C_6H_2Cl_2(OH)_2$, crystallises in flat, long leaflets melting at 164°. The *diacetyl-derivative* forms slender needles melting at 98°, and soluble in the usual solvents.

When alcoholic potash (10 per cent.) is dropped into an alcoholic solution of metadichloroquinone, the liquid becomes first green, and then brownish-red, but as soon as the potash is in excess, the colour begins to fade; red crystals of a potassium salt are then deposited, the yield being 5—6 per cent. of the quinone.

Chlorodiimidoquinol [$(NH)_2 : (OH)_2 : Cl = 1 : 4 : 2 : 5 : 6$] is prepared by dropping strong ammonia into a saturated (at 50—60°) solution of metadichloroquinone, not more ammonia than one quarter of the volume of the quinone solution being added in all. After half an hour, crystals separate, which are washed with alcohol, and purified by crystallisation from glacial acetic acid ; they amount to 20—25 per cent. of the quinone. Chlorodiimidoquinol forms lustrous bronze-coloured, thin, leafy crystals, which sublime without melting, but with partial carbonisation, at 258—260° ; it is insoluble in cold water and alcohol, but dissolves partially in hot alcohol with a violet colour ; it dissolves in strong hydrochloric and sulphuric acid with a blue colour, and is precipitated on dilution. When heated with dilute acids, it loses nitrogen as ammonia, and is converted into a chlorodihydroxyquinone (see below). When heated with potash solution, it is converted into the red *potassium salt* obtained above ; when this is dissolved in water and a slight excess of strong hydrochloric acid added, large, yellow-red, leafy crystals of *chloroparadihydroxyquinone*, $C_6HClO_2(OH)_2$, gradually separate ; this quinone melts at 240°. The *ammonium salt* forms an insoluble, brownish-red, crystalline precipitate when ammonium chloride is added to the solution of the potassinm salt ; the salts of most heavy metals give insoluble brown precipitates under the same circumstances ; the *strontium* and *silver* salts are described.

When chlorine, diluted with carbonic anhydride, is passed through a dilute acid solution of chloroparadihydroxyquinone. chloranilic acid is obtained ; if bromine be used, bromochloranilic acid is formed.

Iodochlorodihydroxyquinone [$O_2 : (OH)_2 : I : Cl = 1 : 4 : 2 : 5 : 3 : 6$] is obtained, as a red, crystalline powder, when a strongly acid solution of the chlorodihydroxyquinone is dropped into the calculated mixture of potassium iodide and iodate ; it is insoluble in cold water, and is decomposed by hot water ; it decomposes at 275° ; hot dilute hydrochloric acid converts it into chloranilic acid with separation of iodine.

Nitroso- and nitro-chloranilic acids are obtained respectively when chloroparadihydroxyquinone is treated with nitrous and nitric acids respectively. These acids are still under investigation.

Chloroparadiamidoquinol hydrochloride, obtained by digesting chlorodiimidoquinol with stannous chloride and hydrochloric acid, crystallises in large, colourless, rhombic octahedra or prisms very soluble in water. The free base has not been obtained.

Tetracetylparadiamidochloroquinol, [$(OAc)_2$: $(NHAc)_2$: Cl = 1 : 4 : 2 : 5 : 6], is obtained by heating the above hydrochloride with acetic anhydride and sodium acetate for half an hour and adding water; it crystallises from hot glacial acetic acid in lustrous, white, four-sided tables, melting at 255°, and sparingly soluble.

Chloroparadiacetamidoquinone [O_2 : $(NHAc)_2$: Cl = 1 : 4 : 2 : 5 : 6] is formed when the above tetracetyl-compound is dissolved in dilute alkali, acidified, and ferric chloride added in slight excess. It crystallises in brilliant, golden needles, melts at 225—226°, and is soluble in hot alcohol and glacial acetic acid. When suspended in ether and treated with hydrochloric acid and stannous chloride, *chloroparadiacetamidoquinol* is formed; this crystallises in colourless prisms melting at about 300°, and soluble in hot water, alcohol, and ether.

A discussion of the constitution of some of the foregoing compounds concludes the paper. A. G. B.

Desmotropy in Phenols. By J. Herzig and S. Zeisel (*Monatsh.*, **10**, 735—769; compare Abstr., 1888, 822; and 1889, 247 and 966).—On adding bromine to tetrethylphloroglucinol in molecular proportion, half the halogen is converted into hydrogen bromide, and a mixture of two isomeric bromotetrethylphloroglucinols is formed. In this operation it is necessary to brominate a solution in absolute alcohol, the presence of water in the alcohol leading to the formation of dibromotetrethylphloroglucinol. The two isomeric monobromotetrethylphloroglucinols are best separated by fractional crystallisation from petroleum (b. p. 60—90°), in which the α-compound is least soluble, and from which it crystallises in thick quadratic plates $a : b : c = 1·0029 : 1 : 1·3749$) melting at 85—88°. The β-compound is more soluble, and crystallises in needles melting at 115—118°. If the α-compound is dissolved in cold potash, soda, or ammonia, and, after remaining some time, precipitated with hydrochloric acid, it is converted into the β-compound; the pure β-compound is, however, not always the most stable form, for when a solution in acetic acid is precipitated with water, a mixture of the α- and β-compounds is obtained. If the acetic acid solution is boiled, the conversion of the β- into the α-compound takes place completely, and the same result is produced on boiling a solution of the β-compound in benzene or some other solvent without chemical action on it. Sodium β-bromotetrethylphloroglucinol, $C_{14}H_{20}BrO_3Na$, is obtained in long, colourless crystals, readily soluble in water, on dissolving the β-compound in a small excess of pure caustic soda; the potassium salt much resembles it; the silver salt is crystalline and soluble in water and in alcohol. The α-compound furnishes the same salts.

On heating with acetic anhydride, both α- and β-bromotetrethylphloroglucinol gave the same monacetate, $C_{14}H_{20}BrO_3Ac$, which crystallises in monoclinic prisms ($a : b : c = 1·7 : 1 : x$) and melts at

66—68°. When β-potassium bromotetrethylphloroglucinol is heated with an excess of ethyl iodide for three hours, ethyliodotetrethylphloroglucinol, crystallising from petroleum in asymmetric plates ($a : b : c = 1 : 1\cdot0941 : 0\cdot8947$) and melting at 51—53°, is formed. Both α- and β-bromotetrethylphloroglucinol give the same tetrethylphloroglucinol (m. p. 210—212°) on reduction with zinc, and the same dibromide on bromination in dilute alcoholic solution. The dibromide melts at 80—82°, crystallises from dilute alcohol in flat needles of considerable length, contains no hydroxyl-group, and gives, on reduction with zinc and acetic acid, tetrethylphloroglucinol (m. p. 209—211°), and on heating with acetic anhydride, the above described monacetate.

The general behaviour of the isomeric bromotetrethylphloroglucinols leads the authors to attribute the constitution

$$[O : Et_2 : O : Et_2 : O : H,Br = 1 : 2 : 3 : 4 : 5 : 6],$$

to the α-compound, and $[OH : Et_2 : O : Et_2 : O : Br = 1 : 2 : 3 : 4 : 5 : 6]$ to the β-compound; the dibromide produced from both being formed by isomeric change, and represented by the constitution

$$[O : Et_2 : O : Br_2 : O : Et_2 = 1 : 2 : 3 : 4 : 5 : 6].$$

G. T. M.

Constitution of Asarone. By J. F. Eykman (*Ber.*, **22**, 3172—3176).—The vapour-density of asarone, the crystalline constituent of asarum oil, determined under reduced pressure, was found to be 102·9; an optical examination of a mixture of asarone and safrole showed that asarone contains a propenyl- and not an allyl-group. The constitution of asarone is therefore $[(OMe)_3 : C_3H_5 = 1 : 2 : 5 : 4]$, where $C_3H_5 = CH{:}CHMe$.

The liquid constituent of asarum oil is probably a methyl ether of isoeugenol. F. S. K.

New Sugar with an Aromatic Nucleus. By Maquenne (*Compt. rend.*, **109**, 812—814).—A commercial sugar, *pinite*, derived from the resin of the *Pinus lambertiana* of Nebraska, resembles the pinite described by Berthelot which was derived from the same source, but differs from it in melting point and rotatory power. Both are very soluble in water, slightly soluble in alcohol, crystallise in nodules, and have a high rotatory power. Berthelot's pinite has a rotatory power of $[\alpha]_j = +58\cdot6$; the new sugar, which the author distinguishes as β-pinite, has a rotatory power $[\alpha]_D = 65°\cdot51$ and melts at 186—187° (corr.). It has the same melting point and rotatory power as sennite, and probably is identical with it.

β-Pinite has a composition intermediate between $C_7H_{14}O_6$ and $C_8H_{16}O_7$. When boiled for a short time with fuming hydriodic acid, it yields methyl iodide and a sugar, $C_6H_{12}O_6$, which crystallises in small tetrahedra, melts at 246° (corr.), dissolves very readily in water, and is almost insoluble in alcohol and quite insoluble in ether. Cryometric estimation of its molecular weight gave the numbers 176—178, so that it is isomeric with glucose. When heated with nitric acid, it yields rhodizonic acid, which can be converted into tetrahydroxyquinone by the action of hydrochloric acid. It follows

from these results that β-pinite is the methyl salt of the sugar $C_6H_{12}O_6$, and the latter is a benzene-derivative isomeric with inosite; it may be distinguished as β-inosite.

Berthelot's pinite also yields methyl iodide and β-inosite when treated with hydriodic acid. C. H. B.

Lactones derived from Glycines. By P. W. ABENIUS (*J. pr. Chem.* [2], **40**, 498—504: compare Abstr., 1888, 825).—*Glycolylphenylglycine*, $OH\cdot CH_2\cdot CO\cdot NPh\cdot CH_2\cdot COOH$, is prepared by heating chloracetophenylglycocine with aqueous soda for half an hour, adding excess of hydrochloric acid, and extracting with ether; by distilling the ether and crystallising the residue from a mixture of benzene and alcohol, the new glycine is obtained in large, transparent, rhombic tables melting at 127—128°, soluble in water and alcohol, and sparingly in ether and benzene. The *calcium salt* (with 6 mols. H_2O) and the *barium salt* (with 7 mols. H_2O), are described.

Anhydroglycolylphenylglycine, $NPh<\begin{matrix}CO\cdot CH_2\\ CH_2\cdot CO\end{matrix}>O$ (compare Knorr's phenylmorpholine, Abstr., 1889, 1219), is obtained by heating glycolylphenylglycine at 160°; it crystallises from hot alcohol in silky needles which melt at 169° and dissolve with difficulty.

Glycolylphenylglycinamide, $OH\cdot CH_2\cdot CO\cdot NPh\cdot CH_2\cdot CONH_2$, obtained by passing dry ammonia through an alcoholic solution of the last-mentioned compound, crystallises in lustrous leaflets, melts at 128—129° and dissolves easily in water and alcohol, but only sparingly in benzene.

Glycolylorthotolylglycine and anhydroglycolylorthotolylglycine have been described before (Abstr., 1888, 825); the *potassium salt* (with 1 mol. H_2O), the *silver salt*, and the *barium salt* (with 7 mols. H_2O) of the former are here described.

Glycolylorthotolylglycinamide, $OH\cdot CH_2\cdot CO\cdot N(C_6H_4Me)\cdot CH_2\cdot CONH_2$, obtained from the latter in like manner to glycolylphenylglycinamide, crystallises in rhombic tables and melts at 152°. A. G. B.

Metaphenylenediamine from Resorcinol. By A. SEYEWITZ (*Compt. rend.*, **109**, 814—817).—Resorcinol is heated in sealed tubes at 280—300° for three hours with four times its weight of anhydrous (but not fused) calcium chloride, previously saturated with dry ammonia. The product is agitated with twenty times its weight of cold water for ten minutes, filtered, the amine extracted with ether after addition of a slight excess of potassium hydroxide, and the ethereal solution saturated with dry hydrogen chloride, which precipitates crystals of metaphenylenediamine hydrochloride in quantity amounting to about 60 per cent. of the resorcinol taken. No unaltered resorcinol is left in the tube. The amine is not formed below 200°, and even at 250° some resorcinol remains unaltered. Direct experiments show that the maximum yield is obtained by heating for three hours at 300°; longer heating reduces the quantity of diamine obtained. C. H. B.

Condensation-products of Carbodiimides and Orthodiamines. By I. Moore (*Ber.*, **22**, 3186—3201; compare Abstr., 1889, 983).—*Dimethyldiphenyldiamidomethyleneorthophenylenediamine*, $C_{19}H_{16}N_4Me_2$, prepared by boiling the phenylene-base with methyl iodide and potash in alcoholic solution, crystallises from alcohol in colourless needles or prisms and decomposes at about 200°, but without melting; it is readily soluble in hot benzene and hot alcohol, but only sparingly in boiling water, and almost insoluble in ether. The *tetranitroso*-compound, $C_{19}H_{14}N_4(NO)_4$, separates in slender needles when the base is treated with sodium nitrite in well-cooled glacial acetic acid solution; it gradually decomposes at about 110°, melts at about 137—138°, and is readily soluble in ether, glacial acetic acid, hot benzene, and alcohol, but insoluble in water. It dissolves freely in warm dilute hydrochloric acid and dilute sulphuric acid, and it gives Liebermann's nitroso-reaction.

Diacetyldiparatolyldiamidomethyleneorthophenylenediamine,

$$C_{21}H_{20}N_4Ac_2,$$

prepared by warming the paratolyl-base (*loc. cit.*) with acetic anhydride, crystallises from warm dilute alcohol in colourless needles, melts at 142—143°, and is readily soluble in alcohol, benzene and ether, but almost insoluble in light petroleum. The *dibenzoyl*-derivative, $C_{21}H_{20}N_4Bz_2$, is obtained when the base is heated with benzoic anhydride at 130—140° for an hour; it crystallises from boiling alcohol in colourless needles or slender prisms, melts at 184—185°, and is readily soluble in hot alcohol and hot benzene, but only sparingly in ether and almost insoluble in light petroleum. The *tetrabenzoyl*-derivative, $C_{21}H_{18}N_4Bz_4$, prepared by heating the base with benzoic anhydride at 240—250° for $2\frac{1}{2}$ hours, crystallises from boiling alcohol in colourless, slender needles, melts at 273—274°, and is readily soluble in boiling cumene, moderately easily in hot alcohol and benzene, and almost insoluble in light petroleum. The *tetranitroso*-derivative, $C_{21}H_{18}N_4(NO)_4$, crystallises in slender, yellow needles, gradually decomposes at about 120° and melts at about 130°; it is readily soluble in alcohol, ether, and warm benzene, but almost insoluble in light petroleum. It gives Liebermann's nitroso-reaction.

Tetraphenyldiamidodimethyleneorthophenylenediamine, $C_{32}H_{28}N_6$, is obtained when diphenyldiamidomethyleneorthophenylenediamine is heated at 200° with carbodiphenylimide. It crystallises in colourless, well-defined rhombic prisms, $a : b : c = 0.6633 : 1 : 0.5685$, melts at 138—139°, and is readily soluble in alcohol, ether, and benzene, but almost insoluble in light petroleum. When distilled, it is decomposed into aniline and diphenyldiamidomethyleneorthophenylenediamine; it is also decomposed by 20 per cent. hydrochloric acid at 150°, yielding diphenylcarbamide and phenylenediamine. The *hydrochloride*, $(C_{32}H_{28}N_6)_2,3HCl$, crystallises in thin, colourless plates and is readily soluble in alcohol and hot water. The *platinochloride* $(C_{32}H_{28}N_6)_4,3H_2PtCl_6$, which crystallises in orange-red plates, is only sparingly soluble in hot alcohol and insoluble in water and ether. The *sulphate*, $C_{32}H_{28}N_6,2H_2SO_4$, crystallises from alcohol

in colourless, prismatic needles and is readily soluble in hot alcohol and hot water, but insoluble in ether. The *tetramethyl*-derivative, $C_{32}H_{24}N_6Me_4$, crystallises from warm benzene in colourless, prismatic needles, melts at 181—182°, and is readily soluble in warm alcohol, ether, and benzene, and in mineral acids. The *tetracetyl*-derivative, $C_{32}H_{24}N_6Ac_4$, crystallises from a mixture of benzene and light petroleum in colourless, well-defined prisms, melts at 125—126°, and is readily soluble in alcohol, ether, and benzene, but only sparingly in light petroleum. The *tetrabenzoyl*-derivative, $C_{32}H_{24}N_6Bz_4$, crystallises from hot alcohol in small, colourless needles or prisms, melts at 181—182°, and is readily soluble in hot alcohol and benzene, but only sparingly in ether, and almost insoluble in light petroleum.

Tetraparatolylamidodimethyleneorthophenylenediamine, $C_{36}H_{36}N_6$, can be prepared by heating orthophenylenediamine (1 mol.) with carbodiparatolylimide (1 mol.) at 130—140°, and then adding a further quantity (1 mol.) of the imide and heating again for 3—4 hours at 200°. It crystallises from hot alcohol in colourless needles, melts at 115—116°, and is readily soluble in hot alcohol and benzene, but only very sparingly in ether and light petroleum. It dissolves in concentrated sulphuric acid, yielding a colourless solution, and it is decomposed by 30 per cent. hydrochloric acid at 150°, yielding orthophenylenediamine and diparatolylcarbamide. The *hydrochloride*, $(C_{36}H_{36}N_6)_2,3HCl$, crystallises from dilute hydrochloric acid in colourless, prismatic needles and is readily soluble in alcohol and hot water, but only very sparingly in ether, and insoluble in benzene. The *platinochloride* $(C_{36}H_{36}N_6)_2,3H_2PtCl_6+15H_2O$ separates in orange-red plates when platinic chloride is added to a dilute hydrochloric acid solution of the base; it loses its water at 100° and is insoluble in water, ether, and benzene, but readily soluble in warm alcohol. The *sulphate*, $C_{36}H_{36}N_6,2H_2SO_4$, crystallises in colourless needles and is readily soluble in hot alcohol and hot water, but almost insoluble in benzene and ether. The *tetracetyl*-derivative, $C_{36}H_{32}N_6Ac_4$, separates from benzene in small, granular crystals, melts at 114—115°, and is readily soluble in alcohol, hot benzene, and hot light petroleum, but very sparingly in cold ether. The *tetrabenzoyl*-derivative, $C_{36}H_{32}N_6Bz_4$, crystallises from alcohol in colourless needles, melts at 145—146°, and is readily soluble in hot alcohol, ether, and benzene, but almost insoluble in light petroleum. F. S. K.

Pentamidobenzene. By A. W. PALMER and C. L. JACKSON (*Amer. Chem. J.*, 11, 448—456; compare Abstr., 1888, 825, and A. Barr, *ibid.*, 822).—*Triamidodinitrobenzene*, $C_6H(NH_2)_3(NO_2)_2$, was prepared by heating tribromodinitrobenzene, melting at 192°, with alcoholic ammonia at 100° under pressure. It was obtained in two forms—in reddish-yellow needles and in black, amorphous masses; it does not melt even above 300°, but is decomposed if heated more intensely, and is insoluble in most ordinary solvents, but dissolves slightly in alcohol and in chloroform, from which solutions it crystallises in small, yellow plates. When reduced with tin and hydrochloric acid, it yields a *trihydrochloride of pentamidobenzene*, $C_6H(NH_2)_2(NH_3Cl)_3$; this crystallises in small, colourless, rhombic plates, turning brown after a

time, and forming a tarry substance when heated with hot water or oxidising agents. This substance is sparingly soluble in alcohol, and dissolves easily in water, from which it is precipitated by passing in hydrogen chloride; it is insoluble in ether, benzene, and chloroform. The free base cannot easily be prepared from it. Evidence was also obtained of the formation of a pentahydrochloride of this base. *Trianilidodinitrobenzene*, $C_6H(NHPh)_3(NO_2)_2$, was also prepared by heating aniline with tribromodinitrobenzene; it melts at 179° and crystallises from alcohol in orange-red needles, from ether in groups of short prisms; from solution in benzene or chloroform it is deposited in an amorphous form. It dissolves readily in benzene, chloroform, and hot alcohol, moderately in ether, carbon bisulphide, acetic acid, and acetone. It is not acted on by hydrochloric acid, but dissolves in nitric and sulphuric acids, forming yellow solutions. This research has been discontinued owing to the publication of a paper by Barr on the same subject. C. F. B.

Action of Carbon Bisulphide on certain Azo-compounds and Hydrazones. By P. JACOBSON and V. SCHENCKE (*Ber.*, 22, 3232—3245).—It has previously been shown by Jacobson (Abstr., 1888, 487) that by the action of carbon bisulphide on benzeneazo-β-naphthol, two anhydro-compounds of α-amido-β-naphthol are formed, namely, *thiocarbamidonaphthol*, $C_{10}H_6<{}^{O}_{N}>C\cdot SH$, and *carbanilamidonaphthol*, $C_{10}H_6<{}^{O}_{N}>C\cdot NHPh$. The authors have examined the action of carbon bisulphide on benzeneazoparacresol, benzeneazopseudocumenol, and benzenedisazoresorcinol, and find that in all these cases the reaction proceeds in a manner exactly analogous to that described above. They have also extended their experiments to the hydrazones of β-naphthaquinone and phenanthraquinone, and show that the same reaction takes place in these cases also. The results obtained form, therefore, a further confirmation of the supposition that the atoms in the characteristic groups of these azo-compounds and orthoquinonehydrazones are combined together in the same manner; whereas, from their modes of formation, it would be expected that the groups would be represented by the formulæ $\begin{matrix}\cdot C\cdot OH\\ \| \\ \cdot C\cdot N{=}N\cdot Ph\end{matrix}$ and $\begin{matrix}\cdot C{=}O\\ | \\ \cdot C{=}N{-}NHPh\end{matrix}$ respectively. Between the various constitutional formulæ which have been proposed, this reaction, which occurs at a high temperature, cannot of course decide.

In carrying out the reaction, 1 part of the azo-compound or hydrazone is heated with 2—3 parts of carbon bisulphide in a sealed tube for eight hours. The temperature necessary is 190—210°, except in the case of benzenedisazoresorcinol, when the reaction takes place at 150—155°, but proceeds less smoothly than with the other compounds.

The products of the reaction of benzeneazoparacresol and carbon bisulphide are *thiocarbamidocresol*, $C_6H_3Me<{}^{O}_{N}>C\cdot SH$, and *carbanil-*

amidocresol, $C_6H_3Me<^{O}_{N}>C\cdot NHPh$. The former crystallises from dilute alcohol in colourless, stellar aggregates of needles, melting at 216—217°. The second compound crystallises from the same solvent in long, colourless needles which melt at 205—206°. Its *picrate* melts at 216—217°, and its *acetyl*-compound at 86—87°.

The first product of the reaction of benzeneazopseudocumenol and carbon bisulphide, *thiocarbamidocumenol*, $C_6HMe_3<^{O}_{N}>C\cdot SH$, crystallises in colourless needles melting at 252—253°. By the action of iodine on its sodium salt, it is converted into the *bisulphide*, $S_2[C<^{O}_{N}>C_6HMe_3]_2$, which separates from chloroform solution in colourless, prismatic crystals melting at 150—151°. The second compound formed, *carbanilamidocumenol*, $C_6HMe_3<^{O}_{N}>C\cdot NHPh$, crystallises in broad, colourless needles melting at 145°. Its *picrate* melts at 197—198°.

The products of the reaction of benzenedisazoresorcinol and carbon bisulphide are more difficult to purify than those previously mentioned. The first, *thiocarbodiamidoresorcinol*, $C_6H_2[<^{O}_{N}>C\cdot SH]_2$, forms an amorphous, yellowish-white powder, which commences to blacken at 250°, and melts with decomposition at 270°. *Carbanildiamidoresorcinol*, $C_6H_2[<^{O}_{N}>C\cdot NHPh]_2$, is likewise an amorphous powder, which blackens at 240°, and melts with complete decomposition at 270°. It unites with 2 mols. of picric acid forming a picrate which melts above 240°.

The two compounds obtained by the reaction of naphthaquinonehydrazone and carbon bisulphide are isomeric with those obtained from benzeneazo-β-naphthol, in which the nitrogen and oxygen atoms are in the α- and β-positions respectively. In the compounds to be described these positions are reversed. *Thiocarbamido-α-naphthol*, $C_{10}H_6<^{N}_{O}>C\cdot SH$, crystallises in long, colourless needles, which melt with decomposition at 259—260°, and are readily soluble in warm alcohol, acetic acid, and benzene. It is converted by potassium ferricyanide into the *bisulphide*. The second compound, *carbanilamido-α-naphthol*, $C_{10}H_6<^{N}_{O}>C\cdot NH\cdot Ph$, crystallises from chloroform in colourless needles melting at 232—233°, and is easily soluble in benzene, alcohol, and acetic acid. Its *picrate* forms microscopic prisms and melts at 213—214°.

Phenanthraquinonehydrazone and carbon bisulphide.—*Thiocarbamidophenanthrol*, $C_{14}H_8<^{O}_{N}>C\cdot SH$, is formed in very small quantity, and is an amorphous, colourless powder. *Carbanilamidophenanthrol*, $C_{14}H_8<^{O}_{N}>C\cdot NHPh$, crystallises from glacial acetic acid in pale-yellow needles, united to stellate aggregates, which melt at

192—193°. It is readily soluble in alcohol and benzene, less so in acetic acid, and is resolved by alcoholic potash into aniline, ammonia, carbonic anhydride, and hydrophenanthraquinone. Its *picrate* forms microscopic prisms melting at 235—236°, and its *acetyl*-derivative crystallises in small, colourless plates, and melts at 163—164°.

The hydrazones of orthodiketones (formerly regarded as mixed azo-compounds) do not act in this manner with carbon bisulphide. Parahydroxyazo-compounds are attacked, but resinous products are formed. Azobenzene, on the other hand, is converted at 280—300° into the compound $C_6H_4<^{N}_{S}>C\cdot SH$, described by Hofmann (Abstr., 1887, 823).

H. G. C.

Ethylenephenylhydrazine. By O. BURCHARD (*Annalen*, **254**, 115—128; compare Abstr., 1889, 138).—α-Ethylenephenylhydrazine (m. p. 90·5°) dissolves in concentrated sulphuric acid, and on adding a trace of nitric acid an intense purple-red coloration is produced. When it is treated with sodium nitrite in dilute hydrochloric acid solution, nitrosoethylenediphenyldiamine (m. p. 160°) is precipitated. The *sulphate*, $C_2H_4(NPh\cdot NH_2)_2,H_2SO_4$, crystallises from dilute alcohol in colourless needles, and is only sparingly soluble in alcohol. The *nitrate*, $C_2H_4(NPh\cdot NH_2)_2,2HNO_3$, crystallises from alcohol in colourless needles or plates, is readily soluble in water, and melts at 172—173° with decomposition. The *oxalate*, $C_2H_4(NPh\cdot NH_2)_2,C_2H_2O_4$, crystallises in needles melting at 183° with decomposition. The *diacetyl*-derivative, $C_2H_4(NPh\cdot NHAc)_2$, crystallises from alcohol in slender, colourless needles, melts at 222°, and is readily soluble in glacial acetic acid, but only sparingly in cold alcohol, and insoluble in ether.

Ethylenephenylhydrazinedisuccinic acid,

$$C_2H_4(NPh\cdot CO\cdot C_2H_4\cdot COOH)_2,$$

prepared by heating the hydrazine (1 mol.) with succinic anhydride (2 mols.) in alcoholic solution, separates from dilute alcohol in colourless crystals, melts at 203°, and is almost insoluble in alcohol, but readily soluble in water. The *sodium* salt is crystalline; the *lead* salt separates from hot water, in which it is only very sparingly soluble, in the form of a crystalline powder.

Succinylethylenephenylhydrazine, $C_2H_4<^{NPh\cdot NH\cdot CO}_{NPh\cdot NH\cdot CO}>C_2H_4$, is obtained when the hydrazine is heated at about 180° with succinic anhydride. It is a colourless powder, readily soluble in alcohol and chloroform, but insoluble in ether; it has no well-defined melting point, as it begins to sinter together at 100—110°, and only becomes completely liquid at about 126°. When boiled with alcoholic potash, it is converted into a compound, probably ethylenephenylhydrazinesuccinic acid, which has acid properties; this substance is a colourless powder, melts at 137—140° with previous softening, and is readily soluble in alcohol, but only very sparingly in ether and chloroform.

Oxalylethylenephenylhydrazine, $C_2H_4<^{NPh\cdot NH\cdot CO}_{NPh\cdot NH\cdot CO}$, prepared by

heating the oxalate at about 183°, is a colourless, amorphous powder soluble in alcohol.

Ethylenetriphenylthiosemicarbazide,

$$NHPh\cdot CS\cdot NH\cdot NPh\cdot C_2H_4\cdot NPh\cdot NH_2,$$

separates as an oil when an alcoholic solution of the hydrazine is warmed with phenylthiocarbimide; it crystallises from alcohol in slender needles, melts at 164·5°, and is moderately easily soluble in alcohol.

Ethylenetetraphenyldithiosemicarbazide, $C_2H_4(NPh\cdot NH\cdot CS\cdot NHPh)_2$, is a crystalline powder, melts at 194·5°, and is sparingly soluble in alcohol.

Acetonethylenephenylhydrazine, $CMe_2{:}N\cdot NPh\cdot C_2H_4\cdot NPh\cdot NH_2$, prepared by boiling the hydrazine with acetone in alcoholic solution, crystallises from alcohol in colourless plates, melts at 71—72°, and has basic properties. The *acetophenone* condensation-product, $C_2H_4(NPh\cdot N{:}CMePh)_2$, crystallises from alcohol in golden needles, melts at 117—118°, and is only sparingly soluble in alcohol.

Attempts to prepare condensation-products with dialdehydes and diketones were unsuccessful. F. S. K.

Oximes. By H. GOLDSCHMIDT (*Ber.*, **22**, 3101—3114).—*Carbanilidobenzaldoxime*, $CHPh{:}N\cdot O\cdot CO\cdot NHPh$, is obtained when benzaldoxime (1 mol.) is warmed with phenylcarbimide (1 mol.) in benzene solution. It crystallises from benzene, alcohol, and ether in colourless needles, melts at 135—136°, and is decomposed when heated above its melting point, yielding diphenylcarbamide, benzonitrile, water and carbonic anhydride; other carbanilidoximes give analogous decomposition-prodncts under the same conditions. When warmed with alcoholic potash, it is decomposed into benzaldoxime and ethyl phenylcarbamate, and when boiled with alkalis, it yields benzaldoxime and aniline.

Carbanilidoanisaldoxime, $OMe\cdot C_6H_4\cdot CH{:}N\cdot O\cdot CO\cdot NHPh$, crystallises from benzene in long needles melting at 82°.

Dicarbanilidosalicylaldoxime,

$$NHPh\cdot CO\cdot ON{:}CH\cdot C_6H_4\cdot O\cdot CO\cdot NHPh,$$

crystallises from benzene in small scales melting at 115°.

Carbanilidofurfuraldoxime, $C_4H_3O\cdot CH{:}N\cdot O\cdot CO\cdot NHPh$, crystallises from benzene in needles melting at 138°.

Carbanilidoacetoxime, $CMe_2{:}N\cdot O\cdot CO\cdot NHPh$, crystallises from benzene in needles and melts at 108°.

Carbanilidoacetophenoneoxime, $CMePh{:}N\cdot O\cdot CO\cdot NHPh$, crystallises in small, colourless needles, and melts at 126°.

Carbanilidobenzophenoneoxime, $CPh_2{:}N\cdot O\cdot CO\cdot NHPh$, crystallises from benzene in colonrless, microscopic needles melting at 176°.

Carbanilidocarvoxime, $C_{10}H_{14}{:}N\cdot O\cdot CO\cdot NHPh$, crystallises from benzene in prisms and melts at 130°. The corresponding derivative of isocarvoxime crystallises from benzene in needles melting at 150°.

Carbanilidocamphoroxime, $C_{10}H_{16}{:}N\cdot O\cdot CO\cdot NHPh$, crystallises from benzene in needles and melts at 94°; it is decomposed when heated

at 120—130°, yielding diphenylcarbamide, campholenenitrile, carbonic anhydride, and water.

Propionaldoxime and valeraldoxime combine with phenylcarbimide with development of heat, yielding oily compounds; mesityleneoxime also gives an oily product.

Carbanilidoquinoneoxime, $C_6H_4O{:}N{\cdot}O{\cdot}CO{\cdot}NHPh$, crystallises in short, yellow prisms, begins to decompose at about 110°, and decomposes completely at 160°, but without melting. It is decomposed by boiling alcohol, yielding quinoneoxime, and when treated with alkalis it is decomposed into quinoneoxime, aniline, and carbonic anhydride; other carbanilidoximes of this class show a similar behaviour with alkalis.

Carbanilidothymoquinoneoxime, $C_{10}H_{12}O{:}N{\cdot}O{\cdot}CO{\cdot}NHPh$, crystallises in long, yellow needles melting at 131—132°.

Carbanilido-α-naphthaquinoneoxime, $C_{10}H_6O{:}N{\cdot}O{\cdot}CO{\cdot}NHPh$, crystallises in yellow prisms, begins to decompose at about 160°, and melts at 170°.

Carbanilido-β-naphthaquinone-β-oxime, prepared from β-nitroso-α-naphthol, crystallises from benzene (with benzene) in greenish-yellow, microscopic prisms, and decomposes at 119—120°.

Carbanilido-β-naphthaquinone-α-oxime, prepared from α-nitroso-β-naphthol, crystallises in small, yellow needles and melts at 126—128°.

When β-naphthaquinonedioxime (1 mol.) is warmed with phenylcarbimide (2 mols.) in benzene solution, diphenylcarbamide is precipitated and the solution contains β-naphthaquinonedioxime anhydride (m. p. 78°). Toludiquinoyltetroxime is also converted into the anhydride under the same conditions, the phenylcarbimide being converted into diphenylcarbamide.

Carbanilidoisonitrosobutyl methyl ketone, $COMe{\cdot}CPr{:}N{\cdot}O{\cdot}CO{\cdot}NHPh$, crystallises from benzene in colourless plates and melts at 92—93°.

Carbanilidomethylpropylglyoxime, $NOH{:}CMe{\cdot}CPr{:}N{\cdot}O{\cdot}CO{\cdot}NHPh$, is obtained when the preceding compound is treated with hydroxylamine hydrochloride in alcoholic solution; it crystallises from benzene in colourless plates melting at 129—131°.

Dicarbanilidomethylpropylglyoxime,

$$NHPh{\cdot}CO{\cdot}O{\cdot}N{:}CMe{\cdot}CPr{:}N{\cdot}O{\cdot}CO{\cdot}NHPh,$$

prepared by treating methylpropylglyoxime with phenylcarbimide in benzene solution, crystallises in nacreous plates, melts at 164—170° with decomposition, and is only sparingly soluble in warm benzene.

Carbanilido-α-benzilmonoxime, $COPh{\cdot}CPh{:}N{\cdot}O{\cdot}CO{\cdot}NHPh$, prepared from α-benzilmonoxime, crystallises from benzene in small prisms, melts at 144°, and is decomposed when warmed with alkalis, yielding aniline and α-benziloxime; it turns yellow on exposure to light.

Carbanilido-γ-benzilmonoxime, prepared from γ-benzilmonoxime, crystallises from benzene, with ½ mol. of benzene, in colourless needles, loses its benzene at 100°, and melts at 143°; it turns yellow on exposure to light, and is decomposed by alkalis, yielding aniline and the γ-oxime.

Dicarbanilido-α-benzildioxime,

$$NHPh{\cdot}CO{\cdot}O{\cdot}N{:}CPh{\cdot}CPh{:}N{\cdot}O{\cdot}CO{\cdot}NHPh,$$

crystallises in colourless, microscopic plates, melts at 180°, and is only sparingly soluble in the ordinary solvents; it is decomposed by alkalis.

Dicarbanilido-β-benzildioxime crystallises from benzene in small prisms, melts at 187°, and is decomposed by alkalis.

Dicarbanilido-γ-benzildioxime crystallises from benzene in colourless needles containing benzene, and melts at about 175°; when warmed with alkalis, it is decomposed into aniline and benzildioxime anhydride (m. p. 94°).

The fact that all the benziloximes react with phenylcarbimide with equal readiness, yielding compounds of equal stability, is evidence in favour of Auwers' and Meyer's views, namely, that the benziloximes are stereochemically isomeric.

Carbanilidoisobenzaldoxime, $C_{14}H_{12}N_2O_2$, is obtained when isobenzaldoxime (1 mol.) is treated with phenylcarbimide (1 mol.) in ethereal solution, the precipitate quickly separated by filtration, aud recrystallised from cold ether. It separates from benzene in colourless needles, and from ether in quadratic plates melting at 94° with decomposition. It is much more readily decomposed by alkalis than its isomeride (see above), yielding diphenylcarbamide, aniline, and isobenzaldoxime; this behaviour is not in accordance with Beckmann's formula for isobenzaldoxime, neither is the fact that carbanilidoisobenzaldoxime readily undergoes intra-molecular change. When a few bubbles of hydrogen chloride are passed into a cold, saturated benzene solution of carbanilidoisobenzaldoxime it is wholly converted into the isomeride (m. p. 135—136°), some of which separates from the solution in crystals; the same change is brought about, but more slowly, by a trace of phenylcarbimide. F. S. K.

Amidoximes and Azoximes. By F. TIEMANN (*Ber.*, **22**, 3124—3130).—General remarks on the papers of Wurm (this vol., p. 258), Zimmer (next abstract), Stieglitz (next page), and Koch (this vol., p. 260).

Action of Aldehydes on Benzenylamidoxime. By H. ZIMMER (*Ber.*, **22**, 3140—3147).—Tiemann has shown (this vol., p. 44) that acetaldehyde forms a condensation-product with benzenylamidoxime. The author has extended this reaction to other aldehydes.

Benzenylhydrazoximephenylethylidene, $CPh{<}{\genfrac{}{}{0pt}{}{N\cdot O}{NH}}{>}CH\cdot CH_2Ph$, is formed when phenylacetaldehyde acts on benzenylamidoxime. It forms small, white needles sparingly soluble in boiling water, easily so in ether, chloroform, and benzene, and melts at 136°. Aqueous hydrochloric acid resolves the compound into its components, but dry hydrogen chloride forms with it a crystalline *hydrochloride*. When oxidised with the calculated quantity of potassium permanganate, the hydrazoxime yields *benzenylazoximephenylethenyl*,

$$CPh{<}{\genfrac{}{}{0pt}{}{N\cdot O}{N}}{>}C\cdot CH_2Ph.$$

This is crystalline, insoluble in water, soluble in alcohol and chloro-

form, sparingly so in ether, and melts at 118°. Neither acids nor alkalis have any action on it.

Benzenylhydrazoximepropylidene, $CPh<\genfrac{}{}{0pt}{}{N\cdot O}{NH}>CHEt$, obtained by the action of propaldehyde on benzenylamidoxime, forms colourless crystals sparingly soluble in water, easily so in organic solvents, and melts at 64°. When heated with alkalis or acids, it is resolved into its components. The *hydrochloride* is crystalline. *Benzenylazoximepropenyl*, $CPh\lessgtr\genfrac{}{}{0pt}{}{N\cdot O}{N}\geqslant CEt$, is a colourless oil boiling at 230—235°. It is soluble in alcohol, insoluble in water. Acids and alkalis are without action on it.

Benzenylhydrazoximeisobutylidene, $CPh<\genfrac{}{}{0pt}{}{N\cdot O}{NH}>CH\cdot CHMe_2$, forms silky needles soluble in boiling water, in organic solvents, and in cold concentrated hydrochloric acid. When heated with acids or alkalis, it is resolved into its components. The *hydrochloride* is crystalline. *Benzenylazoximeisobutenyl* is an oil soluble in alcohol, ether, and chloroform, boils at 253—255°, and is indifferent towards acids and alkalis.

Benzenylhydrazoximeisoamylidene, $CPh<\genfrac{}{}{0pt}{}{N\cdot O}{NH}>CH\cdot CH_2\cdot CHMe_2$, is sparingly soluble in boiling water, easily so in organic solvents, crystallises in colourless needles, and melts at 83°. It is decomposed by hot acids or alkalis, and forms a crystalline *hydrochloride*. *Benzenylazoximeisoamenyl* is an almost colourless oil of slightly aromatic odour, and is soluble in organic solvents. It boils at 257°, and is indifferent to acids and alkalis.

No analogous hydrazo-compound could be obtained from benzaldehyde, dibenzenylazoxime melting at 107° being at once formed.

Benzenylhydrazoximesalicidene, $CPh<\genfrac{}{}{0pt}{}{N\cdot O}{NH}>CH\cdot C_6H_4\cdot OH$, crystallises in colourless needles, and melts at 155°. It is sparingly soluble in water, easily so in organic solvents and in cold alkalis.

Benzenylazoximesalicenyl, $CPh\lessgtr\genfrac{}{}{0pt}{}{N\cdot O}{N}\geqslant C\cdot C_6H_4\cdot OH$, is isomeric with Spilker's salicenylazoximebenzenyl, $OH\cdot C_6H_4\cdot C\lessgtr\genfrac{}{}{0pt}{}{N\cdot O}{N}\geqslant CPh$ (this vol., p. 143), and resembles it in all its properties. It is, therefore, probable that these two compounds are identical, a molecular rearrangement taking place during one or other mode of formation.

The hydrochlorides of all these hydrazoximes are decomposed by water, and are only formed by the action of dry hydrogen chloride.

L. T. T.

Behaviour of Amidoximes towards Diazobenzene-derivatives. By J. STIEGLITZ (*Ber.*, **22**, 3148—3160).—When benzenylamidoxime acts on diazobenzene chloride or sodium diazobenzenesulphonate, diazoamidobenzene and a compound $C_{14}H_{13}N_3O$ are formed. The latter compound seems to be formed from 2 mols. of the amidoxime, the diazo-compound playing the part of determining agent

only, probably acting, as it sometimes does, as a mixture of aniline and nitrous acid. The author has obtained the same compound $C_{14}H_{13}N_3O$ by the action of nitrous acid, and of some mild oxidising agents, though the yields were small. This compound *benzenylhydrazoximeamidobenzylidene*, $CPh{<}{}^{N\cdot O}_{NH}{>}CPh\cdot NH_2$, crystallises in rhombic plates, and melts at 124—125°, being resolved into benzonitrile and benzenylamidoxime. It is insoluble in water, sparingly soluble in ether, moderately so in alcohol, benzene, and chloroform. It has no acid properties, and is only very slightly basic, its unstable *hydrochloride* only being formed when dry hydrogen chloride is passed into a chloroform solution of the base. This salt is soluble in water, but after a time the aqueous solution gradually deposits the free base. It crystallises in colourless, microscopic needles, which melt at 144—145°, and at a few degrees higher temperature decompose into ammonium chloride, dibenzenylazoxime, and small quantities of benzonitrile. The same decomposition takes place very rapidly when the alcoholic solution is boiled. The *platinochloride* forms a pale-yellow precipitate melting at 125·5°, and charring at 130—140°. The *picrate* forms a golden-yellow precipitate, melts at 148—149°, and explodes at a few degrees higher. The free base is not attacked by cold dilute acids or alkalis, but when boiled with alkali is at once resolved into benzonitrile and benzenylamidoxime. When heated with strong aqueous hydrochloric acid at 100°, benzenylamidoxime, benzoic acid, dibenzenylazoxime, and ammonia are formed. Boiling glacial acetic acid, or alcoholic solution of hydrogen chloride, yields dibenzenylamidoxime. The absence of a free oximido-group is shown by ferric chloride giving no coloration. This base is stable towards nitrous acid. Heated with carbon bisulphide at 100°, it yields the compound $C_6H_6N_2S_2$ (Schubart, this vol., p. 49), probably after previous partial decomposition into benzenylamidoxime and benzonitrile. Taking all these facts into consideration, the author considers the above to be its most probable formula.

Orthohomobenzenylhydrazoximeamido-orthohomobenzylidene,

$$C_6H_4Me\cdot C{<}{}^{N\cdot O}_{NH}{>}C(NH_2)\cdot C_6H_4Me,$$

was obtained by the action of sodium diazobenzenesulphonate on orthohomobenzenylamidoxime. It forms colourless, microscopic crystals easily soluble in chloroform, alcohol, and benzene, less so in ether, and insoluble in water and aqueous acids and alkalis. It melts at 109—110°, and although stable at ordinary temperatures, gradually decomposes in hot summer weather into orthotolunitrile and orthohomobenzenylamidoxime. The same decomposition is readily effected by hydrochloric acid at 100°. The author had not enough of this hydrazoxime to prepare *orthohomobenzoyl-orthohomobenzenylamidoxime*, $C_6H_4Me\cdot C(NH_2)\colon N\cdot O\cdot CO\cdot C_6H_4Me$, directly from it, but obtained the latter compound by the action of ortholuic chloride on orthohomobenzenylamidoxime. It crystallises in long, silky needles resembling asbestos, is easily soluble in alcohol, chloroform, ether, and benzene, and in acids, is almost insoluble in water and alkalis, and melts at

117—118°. At 180° water is given off, and *di-orthohomobenzenylazoxime*, $C_6H_4Me\cdot C\ll\genfrac{}{}{0pt}{}{N\cdot O}{N}\gg C\cdot C_6H_4Me$, is formed. This forms very thin, silky needles exceedingly soluble in alcohol, ether, benzene, and chloroform, and melts at 58—59°. It sublimes unchanged, and volatilises in steam or alcohol vapour.

Metanitrobenzenylhydrazoximeamido-metanitrobenzylidene,

$$NO_2\cdot C_6H_4\cdot C<\genfrac{}{}{0pt}{}{N\cdot O}{NH}>C(NH_2)\cdot C_6H_4\cdot NO_2,$$

was obtained by the action of sodium diazobenzensulphonate on metanitrobenzenylamidoxime; it is a pale-yellow substance almost insoluble in the usual solvents. It is most soluble (1 : 2000) in alcohol. It melts at 150—151°. When boiled with alkalis, it is decomposed into the nitrile and amidoxime, but a trace of *metanitrobenzenylazoximemetanitrobenzenyl*, $NO_2\cdot C_6H_4\cdot C\ll\genfrac{}{}{0pt}{}{N\cdot O}{N}\gg C\cdot C_6H_4\cdot NO_2$, is also formed. The latter is, however, best obtained by the action of strong cold sulphuric acid on the hydrazoxime. A mixture of metanitrobenzenylamidoxime and metanitrobenzonitrile gave no trace of the azoxime with sulphuric acid. The azoxime may also be obtained from the hydrazoxime by boiling the latter with glacial acetic acid. It forms microscopic, micaceous needles sparingly soluble in cold organic solvents, melts at 168°, and sublimes unchanged. The author obtained the same compound by acting on metanitrobenzenylamidoxime with metanitrobenzoic chloride.

Attempts to get analogous compounds by the action of diazobenzene chloride on compounds of the general formula $NHR\cdot CPh\colon N\cdot OH$ have as yet proved fruitless.

In the course of his work, the author finds that in the action of hydroxylamine on thiamides and thianilides the presence of excess of alkali is an advantage.

Thiobenzorthotoluide, $CSPh\cdot NH\cdot C_6H_4Me$, is formed by fusing benzorthotoluide with phosphoric pentasulphide. It crystallises from benzene in pale-yellow prisms, and melts at 85—86°. When heated with an alcoholic solution of hydroxylamine hydrochloride, it yields *benzenylorthotoluidoxime*, $NOH\colon CPh\cdot NH\cdot C_6H_4Me$. When excess of alkali is present, the reaction is very much accelerated. This compound crystallises in hexagonal prisms, is easily soluble in acids, alkalis, and organic solvents, and melts at 147°. L. T. T.

Constitution of Benzhydroxamic Acid. By G. MINUNNI (*Ber.*, **22**, 3070—3071).—The compound $N_2HPh\colon CPh\cdot OH$ is formed when benzhydroxamic acid is heated at 130—140° with phenylhydrazine; it crystallises from dilute alcohol in colourless needles, and melts at 165—166°. The formation of this compound shows that benzhydroxamic acid has the constitution $OH\cdot CPh\colon NOH$. F. S. K.

Oils of Wintergreen and Birch. By H. TRIMBLE and H. J. M. SCHROETER (*Pharm. J. Trans.*, **20**, 166—168).—The authors find that the oils of wintergreen and birch are physically and chemically

identical, each consisting of methyl salicylate and small quantities of benzoic acid and ethyl alcohol, together with from 0·3 to 0·447 per cent. of a hydrocarbon of the formula $C_{15}H_{24}$. A sample of artificial oil of wintergreen had the physical, but not the chemical properties of these oils, and was not pure methyl salicylate. R. R.

Methysticin. By C. POMERANZ (*Monatsh.*, **10**, 783—793; compare Abstr., 1888, 1207, and 1889, 278).—This compound exists in the root of *Macropiper methysticum*, from which it may be best prepared by exhaustion with boiling 80 per cent. alcohol; the solution is concentrated and allowed to remain in a cool place for some days, when a crystalline deposit separates, and this on recrystallisation from boiling alcohol furnishes pure methysticin in the form of inodorous, tasteless, prismatic needles melting at 137°. It has the formula $C_{15}H_{14}O_5$, is insoluble in cold water, only slightly soluble in hot water, light petroleum, and ether, but is readily dissolved by boiling alcohol, and cannot be distilled unchanged. On treatment with potash or soda, the compound is dissolved with formation of the potassium or sodium salt respectively of an acid which the author has named *methysticinic acid*. The free acid, $C_{14}H_{12}O_5$, crystallises in yellow, prismatic needles resembling piperic acid, is sparingly soluble in ordinary solvents, dissolves readily in solutions of the alkalis, melts at 180° with evolution of carbonic anhydride, and is coloured red by a solution of ferric chloride. On oxidation with a solution of potassium permanganate, it is converted into a compound identical with Fittig and Remsen's piperonylic acid, $CH_2{:}O_2{:}C_6H_3{\cdot}COOH$ [$O_2 : COOH = 1 : 2 : 4$], which melts at 227°, and gives a characteristic calcium salt.

Methysticol is obtained on boiling methysticinic acid with alkalis or dilute acids. It melts at 94°, is insoluble in alkalis, but is readily dissolved by alcohol or ether, crystallises in flat prisms, forms a compound with phenylhydrazine which melts at 143°, and has the formula $C_{13}H_{12}O_3$.

In consideration of its behaviour with potash, methysticin must be regarded as the methyl salt of methysticinic acid, $CH_2{:}O_2{:}C_6H_3{\cdot}C_7H_7O_3$ [$O_2 : C_7H_7O_3 = 1 : 2 : 4$], the group $C_7H_7O_3$, if methysticinic acid is regarded as a β-ketonic acid, being represented by the chain $-CH{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_2{\cdot}COOH$. The author has not succeeded in detecting the least trace of benzoic acid in the oxidation-product of methysticin (compare Nölting and Kopp, *Mon. Sci.*, 1874, 921). G. T. M.

Tannins. By C. ETTI (*Monatsh.*, **10**, 805—806; compare this vol., p. 164).—Since the tannin $C_{16}H_{14}O_9$, obtained from the aqueous extract of the wood of the Slavonian oak, is a dimethoxy-derivative of a ketonic acid formed by the condensation of 2 mols. of gallic acid, each of which has two hydroxyl-groups placed symmetrically to the carboxyl-group; and since the formation of the ketonic acid must be accompanied by the spliting off of a molecule of water from one of the carboxyl-groups, the ketonic acid must have the constitutional formula $C_6H_2\overset{3,4,5}{(OH)_3}{\cdot}\overset{1}{CO}{\cdot}C_6H\overset{2,3,4}{(OH)_3}{\cdot}\overset{6}{COOH}$.

It has yet to be determined which of the hydroxyl-groups represent the two methoxyl-groups in the tannin. G. T. M.

Ethyl Diphenaeylacetoacetate. By C. PAAL and A. HOERMANN (*Ber.*, **22**, 3225—3232).—Paal has previously shown (Abstr., 1884, 598) that ethyl phenacylacetoacetate (ethyl acetophenoneacetoacetate) is converted by dilute aqueous potash into phenacylacetone. In this reaction, a small quantity of a semi-solid insoluble substance is always obtained, consisting of a crystalline mass, saturated with oil. The latter may be removed by extraction with cold alcohol, and the residue recrystallised from the hot liquid. Two kinds of crystals are thus obtained and can be separated mechanically. The compound present in smaller quantity, $C_{16}H_{13}BrO$, does not combine with phenylhydrazine or hydroxylamine, and is very stable towards reducing agents, but the amount obtained was too small for further examination.

The second compound may be obtained pure by recrystallisation from alcohol, and forms large, transparent monosymmetric tables which have the composition $C_{22}H_{22}O_5$, and consist of *ethyl diphenacylacetoacetate*, $CAc(CH_2\cdot COPh)_2\cdot COOEt$, the ethyl salt of a triketonic acid. It forms large, monosymmetric crystals, $a:b:c = 1\cdot6766 : 1 : 1\cdot1152$; $\beta = 86° 18'$. It melts at 82—83°, is insoluble in water, sparingly soluble in alcohol, but readily in chloroform, acetic acid, and benzene. With phenylhydrazine, it yields a *dihydrazone*, $C_{34}H_{34}N_4O_3$, which forms yellow, crystalline flocks melting at 88—92°, and readily undergoing decomposition. With hydroxylamine it forms, according to the conditions of the experiment, a *mono-*, *di-*, or *trioxime;* all three are amorphous, soluble in alkalis and most organic solvents, but insoluble in water. The mono- and di-oxime melt at 61—63°, and the trioxime at 66—68°.

The ethyl salt is very stable towards aqueous potash, but is readily converted by alcoholic potash into the potassium salt of diphenacylacetic acid, which is identical with the acid previously obtained by Paal and Kues (Abstr., 1887, 261), and yields, with phenylhydrazine, the same derivative, 1-3-diphenyl-5-phenacyl-6-pyridazonephenylhydrazone, $N{<}{\begin{matrix}NPh\cdot CO\\CPh\cdot CH_2\end{matrix}}{>}CH\cdot CH_2\cdot CPh{:}N_2HPh$.

When heated with alcoholic ammonia, diphenylacetic acid is converted into 2 : 6-diphenylpyridine-4-carboxylic acid.

By the action of alcoholic ammonia on ethyl diphenacylacetoacetate, two compounds, melting at 192° and 136° respectively, are obtained, both of which yield one and the same acid on hydrolysis, and appear to be the *amide* and *ethereal salt* of this acid.

H. G. C.

Benzenylazoximemethenylcarboxylic Acid and some of its Derivatives. By A. WURM (*Ber.*, **22**, 3130—3139).—*Ethyl benzenylamidoximeoxalate*, $NH_2\cdot CPh{:}N\cdot O\cdot CO\cdot CO\cdot OEt$, is obtained as a precipitate or oil when a well-cooled chloroform solution of benzenylamidoxime (2 mols.) is added to a similar solution of ethyl chlor-

oxalate (1 mol.). When this substance is separated from the benzenylamidoxime hydrochloride, simultaneously formed, by boiling with water, and subsequently precipitated from alcoholic solution, it forms small, glistening, white needles which decompose suddenly at 118°. It is insoluble in water, chloroform, and benzene, sparingly soluble in ether, and very soluble in alcohol. When digested for some days with water at 100° or saponified with weak alkali, it yields *benzenylamidoximeoxalic acid*, $\mathrm{NH_2{\cdot}CPh{:}N{\cdot}O{\cdot}CO{\cdot}COOH}$, which crystallises in scales soluble in boiling water, and melts at 159°. When the chloroform filtrate from the oxalate is allowed to evaporate spontaneously, *ethyl benzenylazoximemethenylcarboxylate*, $\mathrm{CPh}{<}\substack{\mathrm{N{\cdot}O}\\ \mathrm{N}}{>}\mathrm{C{\cdot}COOEt}$, is obtained. It may also be prepared by heating together benzenylamidoxime and ethyl chloroxalate, and is the substance formed by the sudden decomposition already mentioned of the oximeoxalate; finally it may be prepared by heating the silver salt with ethyl iodide. It crystallises in needles or plates, is moderately soluble in ether and alcohol, readily in chloroform, and very sparingly in cold water. It melts at 51° and distils unchanged at 260°. When hydrolysed, it yields the *free acid*, which crystallises in needles, is soluble in ether and alcohol, sparingly so in cold water, and melts at 98°. It is very slightly volatile in steam, and chars when heated above its melting point. The *potassium* and *calcium salts* are white and crystalline, the *silver* and *lead salts* white powders, the *copper salt* a green powder, and the *methyl salt* (obtained by heating methyl iodide and the silver salt together at 100°) forms pale, silky-white needles which are insoluble in water, but easily soluble in the usual organic solvents; it melts at 38°, and boils at 216°. The *benzyl salt*, obtained by digesting the silver salt with benzyl chloride at 200°, forms long needles soluble in alcohol and ether, insoluble in water; it melts at 105°, turns brown at 210°, and distils with considerable decomposition at 300°. The *amide*, $\mathrm{C_9H_5N_2O_2{\cdot}NH_2}$, is formed when the ethyl salt is digested at 100° with a saturated alcoholic solution of ammonia, or by the action of ammonium carbonate on the chloride. It crystallises in needles insoluble in water and alkali, soluble in organic solvents, and melts at 173°, The *chloride* is prepared by acting on the dry, pure acid with excess of phosphoric oxychloride. It is a clear, limpid liquid with an intensely irritating odour, and boils at 153—155°. It is miscible with chloroform and benzene, is moderately soluble in ether and alcohol, and is heavier than water, in contact with which the chloride is gradually decomposed.

Dibenzenyldiazoximeoxalene, $\mathrm{CPh}{<}\substack{\mathrm{N{\cdot}O}\\ \mathrm{N}}{>}\mathrm{C{-}C}{<}\substack{\mathrm{O{\cdot}N}\\ \mathrm{N}}{>}\mathrm{CPh}$, is obtained by the action at 40° of the above chloride on the sodium salt of benzenylamidoxime suspended in chloroform. It crystallises in very pale, glistening scales which are soluble in alcohol and ether, sparingly so in chloroform, insoluble in ether, and melt at 142°. It dissolves in boiling water without change, and is tolerably stable towards acids and alkalis. This substance is isomeric with Zinkeisen's oxalenediazoximedibenzenyl (this vol., p. 123), and analogous to the succinic derivative obtained by Schulz (Abstr., 1885, 1219). It is prob-

able that during its formation a transitory, intermediate product, $CPh{<}^{N\cdot O}_{-N}{>}C\cdot CO\cdot O\cdot NMe\cdot CPh$, is formed. L. T. T.

Action of Ethyl Chloracetate on Benzenylamidoxime. By H. KOCH (*Ber.*, **22**, 3161—3163).—When ethyl chloracetate (1 mol.) is gradually added to an alcoholic mixture of benzenylamidoxime (1 mol.) and sodium ethoxide (2 mols.), and the whole boiled for three hours, *sodium benzenylamidoximeglycollate* is obtained. This forms white crystals very soluble in water, moderately so in alcohol. Acids liberate from this salt *benzenylamidoximeglycollic acid*,

$$NH_2\cdot CPh{:}N\cdot O\cdot CH_2\cdot COOH.$$

It crystallises in white needles, melts at 123—124°, and is easily soluble in alcohol and ether, sparingly in water. It has both acid and basic properties, dissolving readily in acids and in bases, but its aqueous solution has a strongly acid reaction. When a solution of the acid in hydrochloric acid is boiled for some time the, *anhydride*, $CPh{<}^{N\cdot O\cdot CH_2}_{NH\cdot CO}$, is formed. This internal anhydride is, however, best obtained by heating the acid for some hours at 130—140°. It is easily soluble in alcohol, ether, glacial acetic acid, and boiling water; crystallises in colourless needles, and melts at 148°. It has no longer basic properties, but is still a strong acid, and yields well-developed salts. It is very stable, not being affected by bromine-water or sodium nitrite. Permanganates and analogous oxidising agents readily attack it, benzonitrile being formed. It appears to be analogous in composition and character to benzenylimidoximecarbonyl, $CPh{<}^{N\cdot O}_{NH}{>}CO$. L. T. T.

Oxidation of Paratolyl Benzyl Ketone. By E. BUCHER (*Chem. Centr.*, 1889, ii, 445; from *Arch. sci. phys. nat. Genève*, **22**, 75—76).—The usual oxidising agents split up the paratolyl benzyl ketone molecule; if, however, certain of its bromine-derivatives are heated with water at 180°, better results are obtained. By treating the ketone with bromine in carbon bisulphide, the author has obtained the five bromine substitution-derivatives: *paratolyl bromobenzyl ketone*, $CHPhBr\cdot CO\cdot C_6H_4Me$, melting at 79°; *paratolyl dibromobenzyl ketone*, $CPhBr_2\cdot CO\cdot C_6H_4Me$, melting at 128·5°; *bromoparatolyl dibromobenzyl ketone*, $CPhBr_2\cdot CO\cdot C_6H_4\cdot CH_2Br$, melting at 127°; *dibromoparatolyl dibromobenzyl ketone*, $CPhBr_2\cdot CO\cdot C_6H_4\cdot CHBr_2$, melting at 120°; and *tribromoparatolyl dibromobenzyl ketone*, $CPhBr_2\cdot CO\cdot C_6H_4\cdot CBr_3$, melting at 124°. By heating the dibromo-derivative with water in a sealed tube, the diketone, $COPh\cdot CO\cdot C_6H_4Me$, is obtained, and from the pentabromo-derivative the *diketonic acid*, $COPh\cdot CO\cdot C_6H_4\cdot COOH$, may be prepared by the same treatment. J. W. L.

Azo-colours from Naphtharesorcinol. By S. v. KOSTANECKI (*Ber.*, **22**, 3163—3168).—Believing that Zincke and Thelen's hydr-

oxynaphthaquinonehydrazine (Abstr., 1884, 1359) was really a naphtharesorcinol-derivative, analogous to the nitroso-derivatives lately described by himself, the author has re-examined it. He finds that when heated with acetic anhydride and dry sodium acetate for a few minutes, or even if digested with excess of acetic anhydride for some hours, a *diacetyl-derivative*, $N_2Ph{\cdot}C_{10}H_5(OAc)_2$, is formed, This crystallises from alcohol in needles melting at 122—123°. The formation of only a monacetyl-derivative was one of the chief reasons for Zineke and Thelen's formula, and taking this and its general behaviour into consideration, the author believes this compound to be really phenylazonaphtharesorcinol, $C_{10}H_5(OH)_2{\cdot}N_2Ph$.

When this compound is dissolved in a little alkali, the requisite quantity of sodium nitrite added, and the mixture poured into dilute hydrochloric acid, *nitrosophenylazonaphtharesorcinol*,

$$N_2Ph{\cdot}C_{10}H_4(ON{\cdot}OH){\cdot}OH,$$

is formed. This crystallises in glistening, brownish-red scales, easily soluble in glacial acetic acid, but very sparingly in alcohol and boiling water and alkalis. It dissolves in concentrated sulphuric acid to a dark-green solution; it decomposes at 175°. It dyes mordanted stuffs, but much less intensely than nitrosophenylazoresorcinol. When reduced with tin and hydrochloric acid, it yields amidonaphthalic acid and aniline. This proves that the isonitroso-group has taken the remaining β-position in the nucleus.

When phenylazonaphtharesorcinol is dissolved in excess of alkali, and diazobenzene chloride added, *diphenyldisazonaphtharesorcinol*, $C_{10}H_4(N_2Ph)_2(OH)_2$, is formed. This crystallises in long, red needles, and is insoluble in alkalis, but soluble in chloroform and alcohol; it melts with decomposition at 225°. When reduced with tin and hydrochloric acid, it yields amidonaphthalic acid and aniline, like the above nitroso-compound, and has thus the composition

$$[(N_2Ph)_2:(OH)_2 = 1:3:2:4].$$

It is very similar in appearance and character to the analogous resorcinol-derivative. L. T. T.

Oil of Camphor. By J. TRIMBLE and H. J. M. SCHROETER (*Pharm. J. Trans.*, **20**, 145—148).—A sample of the crude oil of camphor, as obtained from Japan, was found to have a reddish-brown colour, sp. gr. 0·9632 at 16°; it boiled at 180°. The odour resembled that of camphor and sassafras. By fractional distillation, &c., the following definite constituents were isolated from the sample:—

Formula.	Boiling point.	Per cent.
$C_{10}H_{16}$........	150°	0·40
$C_{10}H_{16}$........	159	12·00
$C_{10}H_{16}$........	168	13·00
$C_{10}H_{16}$........	171	5·00
$C_{10}H_{18}O$......	176	15·00
$C_{10}H_{16}$........	180	4·00
$C_{10}H_{16}O$......	204	10·00
$C_{10}H_{18}O_2$.....	213	30·00
$C_{10}H_{10}O_2$.....	232	7·00
$C_{10}H_{12}O_2$.....	247	2·00

The highest-boiling fraction (250—280°; 1·60 per cent.) was a bluish-green oil; the quantity was iusulficient to ascertain if it was a definite substance.

These compounds were fragrant oils, usually colourless, and having high dextro-rotatory powers. The authors also experimented on seven other samples of oil of camphor, which differed considerably from the former in physical properties, and also in the proportionate amounts of the several fractions, some of these being indeed entirely wanting iu certain samples (compare Yoshida, Trans., 1885, 779).

R. R.

Strophanthus Hispidus. By T. R. FRASER (*Pharm. J. Trans.* [3], **20**, 328—335).—This paper is a very detailed account of pharmacological processes and of the reactions of the various extracts obtained from seeds and other parts of Strophanthus. The main results of the author's investigations have already appeared (Abstr., 1888, 606).

Strophanthin melts at 172·5°, dissolves in 55 parts of absolute alcohol, 300 parts of acetone, and 1000 parts of amyl alcohol, and is only very slightly hydrolysed by ptyalin. Strophanthidin is physiologically extremely active. R. R.

Sénégin, from Polygala senega, L. By A. FUNARO (*J. Pharm.* [5], **20**, 450—453; from *Gazzetta*, **19**, 21).—Sénégin, extracted by Gelhen in 1804, was found by Quevenne to yield a white powder, which he named *polygalic acid*. Bolley, in 1855, conclnded that these two substances were identical, and also the same as *saponin*, obtained by Bussy from the root of Saponaria. The author finds five samples of sénégin to give a mean of C = 54·13 ; H = 7·45 ; but these amounts differ notably from Bolley and Quevenne's figures, and also from the results published by Rochleder and by Christophson for saponin. On boiling sénégin with dilute acids, glucose is formed, and a gelatinous substance separates, containing C = 62·26, H = 8·21. These figures are very wide of those obtained for sapogénin, prepared in a crystalline form by Rochleder. The formation of *sénégénin*, $C_{40}H_{32}O_{14}$, and glucose from sénégin is represented as follows: $C_{64}H_{104}O_{34} + 4H_2O = C_{40}H_{64}O_{14} + 4C_6H_{12}O_6$.

The author evidently considers that saponin and sénégin are different compounds, although closely related. J. T.

Pyrroline-derivatives. By C. Paal and N. P. Braikoff (*Ber.*, **22**, 3086—3096).—*Ethyl orthotolyldiphenylpyrrolinecarboxylate*,

$$[C_6H_4Me : COOEt : Ph_2 = 1 : 3 : 2 : 5],$$

prepared by boiling ethyl phenacylbenzoylacetate with orthotoluidine in glacial acetic acid solution, crystallises from alcohol in long, colourless needles, melts at 134—135°, and is readily soluble in alcohol, ether, glacial acetic acid, and benzene. The corresponding *acid*, $C_{24}H_{19}NO_2$, obtained by hydrolysing the ethyl salt with alcoholic potash, crystallises from hot alcohol in colourless scales, melts at 226—227°, sublimes undecomposed, and is only moderately easily soluble in ether, alcohol, and benzene.

Orthotolyldiphenylpyrroline, $C_{23}H_{19}N$, is obtained by distilling the acid over lime; it crystallises from alcohol in flat, colourless needles, melts at 114—115°, boils above 300° without decomposition, and is readily soluble in most organic solvents.

Ethyl paratolyldiphenylpyrrolinecarboxylate crystallises from glacial acetic acid in slender, colourless needles, melts at 145°, and is readily soluble in hot alcohol, benzene, and ether, but only sparingly in light petroleum. The *acid* crystallises from hot glacial acetic acid in small, colourless plates, melts at 205—206°, sublimes without decomposition, and is readily soluble in boiling nitrobenzene, but only sparingly in ether, alcohol, and benzene, and insoluble in light petroleum.

Paratolyldiphenylpyrroline can be prepared, as described in the case of the corresponding ortho-compound; it crystallises from glacial acetic acid in colourless needles, boils without decomposition, and is identical with the substance obtained by Baumann (Abstr., 1887, 736), by distilling paratolylpyrrolinedibenzoic acid over baryta.

Ethyl metaxylyldiphenylpyrrolinecarboxylate $[C_6H_3Me_2 : COOEt : Ph_2 = 1 : 3 : 2 : 5]$, prepared by boiling ethyl phenacylbenzoylacetate with metaxylidine in glacial acetic acid solution, is a thick oily compound. The *acid*, $C_{25}H_{21}NO_2$, crystallises from glacial acetic acid in colourless needles, melts at 253—254°, sublimes undecomposed, and is moderately easily soluble in hot alcohol and benzene.

Metaxylyldiphenylpyrroline, $C_{24}H_{21}N$, crystallises in short, colourless needles, melts at 147—149°, distils without decomposition, and is soluble in most organic solvents.

Ethyl α-naphthyldiphenylpyrrolinecarboxylate, $C_{29}H_{23}NO_2$, crystallises in colourless needles or plates, melts at 181—182°, and is readily soluble in hot alcohol and glacial acetic acid, but only moderately easily in benzene. The *acid*, $C_{27}H_{19}NO_2$, crystallises from glacial acetic acid in colourless plates, melts at 271·5—272°, sublimes undecomposed, and is sparingly soluble in boiling alcohol and benzene, and insoluble in light petroleum. The *potassium* salt is sparingly soluble in boiling water and insoluble in concentrated potash.

α-Naphthyldiphenylpyrroline, $C_{26}H_{19}N$, crystallises from hot alcohol in small, yellowish needles, melts at 148—149°, distils without decomposition, and dissolves freely in most organic solvents when warmed therewith.

Ethyl β-naphthyldiphenylpyrrolinecarboxylate, crystallises from hot alcohol and glacial acetic acid in small, colourless needles melting at

181—182°. The *acid* is obtained by boiling the ethereal salt for a long time with a large excess of alcoholic potash; it crystallises from hot glacial acetic acid in colourless plates, melts above 350°, sublimes undecomposed, and is only sparingly soluble in all ordinary solvents.

β-Naphthyldiphenylpyrroline forms flat, colourless needles or long plates, melts at 207—208°, and is soluble in hot alcohol, glacial acetic acid, and benzene.

Ethyl orthohydroxyphenyldiphenylpyrrolinecarboxylate,

$$OH{\cdot}C_6H_4{\cdot}C_4NHPh_2{\cdot}COOEt,$$

prepared by boiling ethyl phenacylbenzoylacetate with orthamidophenol in alcoholic solution, separates from alcohol or acetic acid in colourless, indented crystals, melts at 158—159°, and is soluble in alkalis and all organic solvents. The *acid*, $C_{23}H_{17}NO_3$, crystallises from glacial acetic acid in colourless, ill-defined needles, melts at 244—245°, sublimes without decomposition, and is readily soluble in ether, alcohol, and glacial acetic acid, but only sparingly in benzene, chloroform, and light petroleum.

Orthohydroxyphenyldiphenylpyrroline, $C_{22}H_{17}NO$, crystallises from glacial acetic acid in yellowish needles, melts at 175—176°, and is readily soluble in ether, alcohol, benzene, and alkalis.

Ethyl paraphenylenedi-diphenylpyrrolinecarboxylate,

$$C_6H_4(C_4NHPh_2{\cdot}COOEt)_2,$$

crystallises from alcohol in yellowish scales, melts at 249—250°, and is soluble in glacial acetic acid and benzene. The *acid*, $C_{40}H_{28}N_2O_4$, separates from hot alcohol in small crystals, melts above 300°, sublimes undecomposed, and is moderately easily soluble in alcohol and glacial acetic acid, but only sparingly in benzene and light petroleum.

F. S. K.

Action of Hydroxylamine on Pyrrolines. By G. CIAMICIAN and C. U. ZANETTI (*Ber.*, **22**, 3176—3179; compare Abstr., 1889, 1208).—Acetonylacetoxime, $NOH{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}NOH$ (m. p., 136·5°, corr.), identical with the compound prepared by Paal (Abstr., 1885, 505), is formed when 2 : 5-dimethylpyrroline is boiled for about six hours with hydroxylamine hydrochloride and sodium carbonate in alcoholic solution. This reaction tends to prove that the compound (m. p., 173°) obtained by treating pyrroline with hydroxylamine (*loc. cit.*) is, in reality, the oxime of succinaldehyde.

When acetonylacetoxime is reduced with sodium and alcohol, it is converted into a *base*, the hydrochloride of which is a colourless, crystalline compound, and has the composition $C_6H_{16}N_2,2HCl$. This base has the same composition as the diamidohexane obtained by Tafel (Abstr., 1889, 976) by reducing the dihydrazone of acetonylacetone.

With hydroxylamine metadimethylpyrroline yields a compound which is soluble in water, and has powerful reducing properties; this new substance is converted into a base $C_6H_{16}N_2$ when it is reduced with sodium and alcohol.

F. S. K.

Derivatives of 1-Hydroxyquinoline. By E. LIPPMANN and F. FLEISSNER (*Monatsh.*, **10**, 794—797).—Amidohydroxyquinoline has been isolated by Fischer and Renouf (Abstr., 1884, 1370), but may be more conveniently prepared from the corresponding nitroso-compound, which is obtained as hydrochloride by adding sodium nitrite (25 grams) to hydroxyquinoline (50 grams) in an aqueous solution containing hydrochloric acid (100 grams). The hydrochloride of the nitroso-compound forms an orange-coloured, crystalline mass, which is only slightly soluble in water, but more soluble in dilute hydrochloric acid; it is decomposed on boiling its aqueous solution, but may be obtained in yellow- or brownish-coloured scales or needles by very careful recrystallisation. With sodium acetate, it gives a gelatinous precipitate which becomes crystalline on standing. Nitrosohydroxyquinoline, $NO{\cdot}C_9NH_5{\cdot}OH$ [= 4 : 1], crystallises from alcohol in pale-yellow or greenish needles, only slightly soluble in benzene, ether, and chloroform, and decomposes on heating to 230°. The *platinochloride*, $(C_9H_6N_2O_2)_2,H_2PtCl_6$, crystallises in brown, glistening scales, and is decomposed on boiling with water. In order to determine the relation of the nitroso-group to the hydroxyl-group, the authors converted it by means of nascent hydrogen into amidohydroxyquinoline, which, on oxidation with potassium dichromate and sulphuric acid, and reduction with sulphurous anhydride, furnished quinol. If the reduction is brought about by means of tin, added a little at a time to a solution of the nitroso-compound in hydrochloric acid, a violent reaction ensues, and a crystalline double salt is obtained. On freeing this from tin by hydrogen sulphide, and adding to the solution sodium acetate, a *dichloramidohydroxyquinoline*, $C_9NH_3Cl_2(NH_2){\cdot}OH$, separates out as a white, crystalline mass, whilst amidohydroxyquinoline remains in solution. The dichloro-derivative crystallises from alcohol, benzene, or chloroform in slender, white, silky needles, which decompose at 160°, and furnishes a hydrochloride crystallising from dilute hydrochloric acid in yellow needles, and readily decomposed by boiling water. If stannous chloride is substituted for the metal, amidohydroxyquinoline is the sole reduction-product, and from this a dihydroxyquinoline sulphate decomposing at 220°, and identical with the compound described by Fisher and Renouf (*loc. cit.*), may be obtained. It must, therefore, be concluded that the nitroso-compound contains the nitroso-group in the para-position relatively to the hydroxyl-group. G. T. M.

Bromoquinolinesulphonic Acids. By A. CLAUS (*J. pr. Chem.* [2], **40**, 444—447).—Bromoquinolinesulphonic acids may be obtained: (1) By synthesis from bromamidobenzenesulphonic acid; (2) by brominating quinolinesulphonic acids; (3) by sulphonating bromoquinolines; (4) by substituting bromine for a hydroxyl-, amido-, &c., group in a hydroxy-, amido-, &c., quinolinesulphonic acid. Of these four possible methods, the third gives the best results. The orientation of the acid is settled by treatment with tin and hydrochloric acid (Lellmann, Abstr., 1888, 296), which produces a hydroquinolinesulphonic acid. The hydroquinolinesulphonic acids are being investigated in the author's laboratory.

Hydroquinoline-4-*sulphonic acid* crystallises in large, rhombic tables, or monoclinic leaflets, which begin to melt at 318° (uncorr.) with decomposition.

Hydroquinoline-1-*sulphonic acid* crystallises in pointed needles, and decomposes at 243° (uncorr.).

Hydroquinoline-3-*sulphonic acid* forms characteristic, glassy, short, monoclinic prisms, the measurements of which are given. It decomposes at 277° (uncorr.).
A. G. B.

Sulphonic Acids of 4′-Bromoquinoline. By A. Claus and W. Schmeisser (*J. pr. Chem.* [2], **40**, 447—454).—4′ : 4-*Bromoquinolinesulphonic acid* is obtained by heating 4′-bromoquinoline with sulphuric acid for some time at 250°—300°; it crystallises from alcohol in beautiful, silky needles, and from water both in long, slender needles (with $1\frac{1}{2}$ mols. H_2O), and in large, anhydrous prisms which become needles when recrystallised from hot water. It is insoluble in ether, decomposes above 300° without melting, and is stable in alkaline solutions. When treated with tin and hydrochloric acid, it is converted into hydroquinoline-4-sulphonic acid. The *potassium salt* (with 1 mol. H_2O), the *sodium salt*, the *calcium salt* (with 7 mols. H_2O), the *barium salt* (with 3 mols. H_2O), the *copper salt* (with 7 mols. H_2O), and the *silver salt* are described. The *ethyl salt* forms transparent needles melting at 125° (uncorr.). The *chloride*, $C_9NH_5Br{\cdot}SO_2Cl$, crystallises from chloroform in needles, and from ether in thick prisms, which melt at 82° (uncorr.). The *amide* forms small, slender needles melting at 255° (uncorr.).

4′ : 2-*Bromoquinolinesulphonic acid* is formed, together with the above 4-sulphonic acid, when 4′-bromoquinoline (1 part) is heated with sulphuric acid (5 parts) containing 30—40 per cent. of sulphuric anhydride for about an hour on the water-bath. If the heating is longer, or the temperature higher, the 2-sulphonic acid is converted into the 4-sulphonic acid. The two acids are separated by crystallising from water, and treating with 96 per cent. alcohol, when the 4-sulphonic acid dissolves. 4′ : 2-Bromoquinolinesulphonic acid crystallises in colourless, rhombic tables, which are sparingly soluble in cold water and insoluble in other solvents; it can be heated to 300° without melting or decomposing. It is not acted on by hot alkalis. Tin and hydrochloric acid convert it into a hydroquinolinesulphonic acid which melts at 255°, and has not yet been described; it is probably *hydroquinoline*-2-*sulphonic acid*. The *sodium salt*, the *potassium salt* (with 1 mol. H_2O), the *barium salt* (with 1 mol. H_2O), the *calcium salt* (with 4 mols. H_2O), the *copper salt* (with 1 mol. H_2O), and the *silver salt* are described. The *ethyl salt* forms short, needle-shaped crystals melting at 100° (uncorr.). The *chloride*, $C_9NH_5Br{\cdot}SO_2Cl$, crystallises from chloroform in colourless needles, and from alcohol in beautiful, lustrous leaflets; it melts at 130° (uncorr.). The *amide* crystallises from hot water in small, white, slender needles melting at 213° (uncorr.), and soluble in alcohol.

When these two acids are brominated, they yield different tribromoquinolines. The 2-sulphonic acid yields a tribromoquinoline

which crystallises in colourless, lustrous prisms melting at 171° (uncorr.); while the 4-sulphonic acid yields a tribromoquinoline which crystallises in slender, colourless needles melting at 300° (uncorr.). A. G. B.

Sulphonic Acids of 4-Bromoquinoline. By A. CLAUS and O. WÜRTZ (*J. pr. Chem.* [2], **40**, 454—460).—When 4-bromoquinoline (1 part) is heated in a flask with sulphuric acid containing 30 per cent. of sulphuric anhydride (5 parts) at 130—140° for 6—8 hours, the 1- and 3-sulphonic acids of 4-bromoquinoline are obtained, the former in considerable quantity, the latter in small quantity. They are separated by crystallising from water, when the 1-sulphonic acid crystallises first. At higher temperatures, disulphonic acids are produced at the same time.

4 : 1-*Bromoquinolinesulphonic acid* crystallises (with 2 mols. H_2O) in colourless, lustrous needles or prisms which dissolve in hot water, but not in cold water or in alcohol. The anhydrous acid is unchanged below 300°. When reduced by tin and hydrochloric acid, it yields hydroquinoline-1-sulphonic acid. The *sodium salt* (with 2 mols. H_2O), the *potassium salt* (with 2 mols. H_2O) the *calcium salt* (with 4 mols. H_2O), the *barium salt* (with 3 mols. H_2O), the *copper salt* (with 5 mols. H_2O), the *silver salt*, and the *lead salt* are described. The *ethyl salt* melts at 110° (uncorr.). The *chloride*, $C_9NH_5Br \cdot SO_2Cl$, crystallises from ether in small, colourless prisms, and from alcohol in tables; it melts at 125° (uncorr.). The *amide* forms small needles melting at 205° (uncorr.), and soluble except in water.

4 : 3-*Bromoquinolinesulphonic acid* crystallises in small, lustrous, colourless, anhydrous needles soluble in alcohol and in water. The *sodium salt* (with 1 mol. H_2O), the *calcium salt* (with 7 mols. H_2O), and the *barium salt* (with 2 mols. H_2O) are described. The *ethyl salt* melts at 130° (uncorr.); the *chloride* melts at 95° (uncorr.); the *amide* forms small, dark-yellow crystals melting at 195° (uncorr.).

When the acid is reduced with tin and hydrochloric acid, it yields hydroquinoline-3-sulphonic acid (?) melting at 171°; and when brominated, it yields a tribromoquinoline melting at 248° (uncorr.). A. G. B.

3 : 1-Bromoquinolinesulphonic Acid and 4 : 3-Nitrobromoquinoline. By A. CLAUS and G. ZUSCHLAG (*J. pr. Chem.* [2], **40**, 460—464).—La Coste (Abstr., 1883, 96) obtained several sulphonic acids by sulphonating parabromoquinoline. The authors, using fuming sulphuric acid (30 per cent. sulphuric anhydride) at 120—125°, only obtained one sulphonic acid.

3 : 1-*Bromoquinolinesulphonic acid* crystallises in beautiful, lustrous, white needles and prisms, which are anhydrous, do not melt at 350°, and are moderately soluble in hot water. The *potassium salt* (with 1 mol. H_2O) and the *silver salt* are described; the *ethyl salt* forms long, colourless, silky needles melting at 139°. When brominated, it yields a *tribromoquinoline* which crystallises in colourless needles, and melts at 185° (uncorr.). Reduction with tin and hydrochloric acid converts it into hydroquinoline-1-sulphonic acid.

La Coste's nitrobromoquinoline (Abstr., 1883, 91) is 4 : 3-*nitro-*

bromoquinoline; it melts at 130° (uncorr.), not 133°; its *hydrochloride*, *platinochloride*, and *methiodide* were obtained.

4 : 3-amidobromoquinoline (*loc. cit.*) melts at 160° (uncorr.), not 164°.

A. G. B.

Hydroxyquinolinesulphonic Acids. By E. LIPPMANN and F. FLEISSNER (*Monatsh.*, **10**, 798—804).—When 1-hydroxyquinoline (1 part) is heated with sulphuric acid (3 parts) in a sealed tube for three hours at 180°, the product is a light-brown syrup which scarcely smells of sulphurous anhydride, and contains a sulphonic acid, $OH\cdot C_9NH_5\cdot SO_3H + 1\frac{1}{2}H_2O$, which crystallises in pale-yellow needles, melts with decomposition at 275°, is only slightly soluble in alcohol, aud is insoluble in ether. The aqueous solution is strongly acid, gives a green coloration with ferric chloride, and an almost insoluble, crystalline precipitate with lead acetate. The potassium salt is anhydrous, and crystallises from water in light, rose-coloured, glistening scales. Its aqueous solution gives a green, granular precipitate with a solution of cupric sulphate, and a crystalline precipitate with mercuric chloride; the silver salt is a crystalline powder; the barium salt is an almost insoluble powder.

Besides the above-described compound, *1-hydroxyquinolinedisulphonic acid*, $OH\cdot C_9NH_4(SO_3H)_2$, is simultaneously formed in small quantities. It may be more readily obtained by heating a mixture of hydroxyquinoline (25 grams), sulphuric acid (75 grams), and phosphoric anhydride (30 grams) at 200° for five hours. It is a very hygroscopic substance, and decomposes at 200°. The hydrogen potassium salt, is a crystalline precipitate; the basic salt, $OK\cdot C_9NH_4(SO_3K)_2$, a compound sparingly soluble in water; the basic copper salt, $Cu[O\cdot C_9NH_4(SO_3)_2Cu]_2 + 10H_2O$, a light-green powder.

G. T. M.

Paradiazine-derivatives. By P. W. ABENIUS (*J. pr. Chem.* [2], **40**, 425—444; compare Abstr., 1889, 134).

Bromacetanilide, $NHPh\cdot CO\cdot CH_2Br$, is obtained by mixing benzene solutions of aniline (2 mols.) and bromacetic bromide (1 mol.), evaporating the benzene at the ordinary temperature, and washing the residue with water, which leaves bromacetanilide undissolved. It crystallises in slender, white needles which melt at 130—131°, and are soluble in alcohol, ether, and benzene, but not in water.

Chloracetylphenylglycine, $CH_2Cl\cdot CO\cdot NPh\cdot CH_2\cdot COOH$, is formed when phenylglycine, suspended in ether, is shaken with an ethereal solution of chloracetic chloride (eq. mols.); the ether is distilled off, and the residue treated with water, when the chloracetylphenylglycine separates as an oil, which soon crystallises. It forms four-sided tables or prisms melting at 132—133°, soluble in alcohol and benzene.

Diphenyldiketodihydroparadiazine, $NPh<\substack{CO\cdot CH_2\\CH_2\cdot CO}>NPh$, is identical with Meyer's phenylglycine anhydride (this Journal, 1878, 294); it may also be obtained by the action of alcoholic potash on bromacetanilide, and by heating chloracetylphenylglycine (1 mol.) with aniline (2 mols.) at 140—150°; this last reaction settles its constitution. It melts at 263°.

Phenylglycinylphenylglycine has been described before (Abstr., 1888, 854; compare Hausdörfer, Abstr., 1889, 1014); it melts at 129—130°.

Bromacetoparatoluidide, $C_6H_4Me\cdot NH\cdot CO\cdot CH_2Br$ [Me : NH = 1 : 4], obtained in the same way as bromacetanilide, crystallises from hot alcohol in long, colourless needles which melt at 164°.

Diparatolyldiketodihydroparadiazine,

$$C_6H_4Me\cdot N<\begin{matrix}CO\cdot CH_2\\CH_2\cdot CO\end{matrix}>N\cdot C_6H_4Me\ [Me : N = 1 : 4],$$

is obtained from bromacetoparatolnidide, or from paratolylglycocine, in the same way as diphenyldiketodihydroparadiazine is obtained from the corresponding phenyl compounds. It crystallises from alcohol in beautiful, long, white needles which melt at 252—253°, and are soluble in glacial acetic acid, but only sparingly solnble in other solvents.

Ethylglycolylparatoluidide, $C_6H_4Me\cdot NH\cdot CO\cdot CH_2\cdot OEt$ [Me : NH = 1 : 4], is obtained as a bye-product in preparing the above paradiazine from bromacetoparatolnidide and alcoholic potash, and may be separated from the mother liquor of the paradiazine by ether, which dissolves it. It crystallises in beautiful, transparent prisms which melt at 32°, and are soluble except in water.

Parabromaceto-xylidide, $C_6H_3Me_2\cdot NH\cdot CO\cdot CH_2Br$ [Me_2 : NH = 1 : 4 : 3], prepared by mixing benzene solutions of paraxylidine (2 mols.) and bromacetic bromide (1 mol.), crystallises in slender, white needles which melt at 145°.

Diparaxylyldiketodihydroparadiazine,

$$C_6H_3Me_2\cdot N<\begin{matrix}CO\cdot CH_2\\CH_2\cdot CO\end{matrix}>N\cdot C_6H_3Me_2\ [Me_2 : N = 1 : 4 : 2],$$

is obtained by the action of alcoholic potash on parabromaceto-xylidide; it crystallises from hot alcohol in beautiful, flat needles melting at 203°, and soluble in benzene and acetic acid, but not in water and ether.

Ethylglycolylparaxylidide, $C_6H_3Me_2\cdot NH\cdot CO\cdot CH_2\cdot OEt$ [Me_2 : NH = 1 : 4 : 2], is extracted by ether from the mother-liquor of the last-mentioned paradiazine; it crystallises in prisms melting at 50°, and solnble in the usual solvents.

Di-α-naphthyldiketodihydroparadiazine,

$$C_{10}H_7\cdot N<\begin{matrix}CO\cdot CH_2\\CH_2\cdot CO\end{matrix}>N\cdot C_{10}H_7,$$

obtained from chloracetonaphthalide and alcoholic potash, crystallises from glacial acetic acid in flat needles melting at 274—275°, and sparingly soluble in alcohol, benzene, and ether.

Methyl metanitrocumate, $NO_2\cdot C_6H_3Pr\cdot COOMe$ [Pr : MeO : NO_2 = 4 : 1 : 3], is obtained by dissolving nitrocumic acid in methyl alcohol and saturating it with hydrogen chloride; it forms large crystals like nitre, which melt at 64°, and are soluble in most solvents.

Methyl metamidocumate is obtained by reducing the nitrocumate with tin and hydrochloric acid; it crystallises in colourless, transpa-

rent prisms or tables melting at 51—52°, and easily soluble except in light petroleum.

Methyl metachloracetamidocumate, $CH_2Cl\cdot CO\cdot NH\cdot C_6H_3Pr\cdot COOMe$ [Pr : COOMe : NH = 4 : 1 : 3], is prepared by mixing benzene solutions of the metamidocumate (2 mols.) and chloracetic chloride (1 mol.), evaporating the benzene at the ordinary temperature, and washing the residue with water, which leaves the chloraceto-derivative undissolved. It crystallises from hot dilute alcohol in long, slender, colourless needles melting at 101—102°, and easily soluble in most solvents except water and light petroleum. If bromacetic bromide be substituted for chloracetic chloride in the above prescription, *methyl metabromacetamidocumate* is obtained; it melts at 106—107°.

Dipropyldiphenyldiketodihydroparadiazinedicarboxylic acid,

$$C_4N_2H_4(C_6H_3Pr\cdot COOH)_2 \ [COOH : Pr : N = 1 : 4 : 3],$$

is prepared by heating alcoholic potash (1 gram) with methyl metachloracetamidocumate (4 grams) in alcohol for half an hour, then adding another gram of potash, and heating for another half hour; the alcohol is now evaporated, the residue treated with water, and an excess of hydrochloric acid added; this throws down a resinous substance, which is washed and heated with alcohol. Part dissolves (see below), leaving the dicarboxylic acid as an insoluble powder, which decomposes before melting, and dissolves in alkalis, being reprecipitated by acids. The *ethyl* salt, obtained by the action of dry hydrogen chloride on an alcoholic solution of the acid, crystallises in flat, lustrous, oblique-ended needles melting at 192—193°, and soluble in alcohol.

Metethylglycolylamidocumic acid, $OEt\cdot CH_2\cdot CO\cdot NH\cdot C_6H_3Pr\cdot COOH$ [COOH : Pr : NH = 1 : 4 : 3], is that portion of the above-mentioned resin which dissolves in alcohol; the alcohol is evaporated, the residue dissolved in potash, reprecipitated by hydrochloric acid, and crystallised from weak alcohol. It forms four-sided tables melting at 140°, and soluble except in water and petroleum.

Phenylorthotolyldiketodihydroparadiazine,

$$NPh{<}{CO\cdot CH_2 \atop CH_2\cdot CO}{>}N\cdot C_6H_4Me \ [Me : N = 1 : 2],$$

is obtained by heating chloracetorthotolylglycine (1 mol.) with aniline (2 mols.) in a sulphuric acid bath at 160°; the product is heated with water and hydrochloric acid, filtered, and the undissolved portion crystallised from alcohol. It forms slender, white needles melting at 165—166°, soluble in hot alcohol and benzene, but insoluble in ether. It forms no platinochloride.

Orthotolylparatolyldiketodihydroparadiazine,

$$C_6H_4Me\cdot N{<}{CO\cdot CH_2 \atop CH_2\cdot CO}{>}N\cdot C_6H_4Me \ [Me : N = 1 : 2 \text{ and } 1 : 4],$$

is obtained by substituting paratoluidine for aniline in the preparation of the last compound. It crystallises in long, white, felted needles melting at 179—180°, soluble in alcohol and benzene, but not in ether.

A. G. B.

Ditriazole-derivatives. By J. A. Bladin (*Ber.*, **22**, 3114—3117; compare Abstr., 1889, 138).

Di-phenylethyltriazole, $\begin{matrix}\mathrm{CEt{\cdot}N} \\ \| \\ \mathrm{N{\cdot}NPh}\end{matrix}\!\!>\!\mathrm{C{\cdot}C}\!<\!\!\begin{matrix}\mathrm{N—CEt} \\ \| \\ \mathrm{NPh{\cdot}N}\end{matrix}$, prepared by boiling cyanophenylhydrazine with excess of propionic anhydride, crystallises from alcohol in prisms, melts at 186·5—187°, and is readily soluble in alcohol, but insoluble in water. The *hydrochloride*, $C_{20}H_{20}N_6,2HCl$, crystallises in microscopic prisms, and is decomposed by water. The *platinochloride* crystallises in orange-yellow, unstable prisms.

Di-diphenyltriazole, $C_{28}H_{20}N_6$, prepared by treating cyanophenylhydrazine with benzoic chloride, crystallises from alcohol in colourless needles, with 2 mols. H_2O, loses its water at 100°, melts at 257—258°, and is only sparingly soluble in alcohol, very sparingly in ether, and insoluble in water; it is a very feeble base.

Di-paratolylmethyltriazole, $C_{20}H_{20}N_6$, is obtained when cyanoparatolylhydrazine is boiled for a few minutes with excess of acetic anhydride. It crystallises from alcohol in long, prismatic needles, melts at 259—260°, and is moderately easily soluble in alcohol, but only sparingly in benzene, and insoluble in water. The *hydrochloride* is readily soluble.

Di-paratolylethyltriazole, $C_{22}H_{24}N_6$, prepared from propionic anhydride in like manner, separates in crystals from alcohol and benzene, in which it is readily soluble, melts at 202—203°, and is insoluble in water.

Di-paratolylphenyltriazole, $C_{30}H_{24}N_6$, prepared from benzoic chloride in like manner, crystallises from alcohol in microscopic needles with 2 mols. H_2O, and from benzene in small plates with 1 mol. of benzene; it melts at about 300°, is insoluble in water, and is only a very feeble base.
F. S. K.

Bases formed by the Action of Potassium Hydroxide on the Halogen-Alkyl Salts of Papaverine. By A. Claus (*J. pr. Chem.* [2], **40**, 465—479).—In this paper the author replies to the recent criticisms of Goldschmiedt (this vol., p. 179) on the work which he (the author) and others have already published on this subject (see Abstr., 1885, 996; 1889, 414).
A. G. B.

Belladonine. By E. Dürkopf (*Ber.*, **22**, 3183—3184).—The brown syrup from which atropine has been obtained (commercially) is a mixture of belladonine, atropine, hyoscyamine, hyoscine, and their decomposition-products tropine, pseudotropine, and tropic acid. When the syrup is boiled with chloroform and ether in acid solution, the hydrocarbons, &c., are removed, and the atropine in the purified base can, by some suitable means, be converted into tropine and tropic acid; the belladonine is not changed by this treatment, but the hyoscine (18—20 per cent.) passes into solution, and can be easily isolated by means of the aurochloride. This salt, $C_{17}H_{23}NO_3,AuCl_3$, crystallises in prisms, melts at 200°, and is sparingly soluble in water.
F. S. K.

Fumarine. By R. REICHWALD (*Zeit. anal. Chem.*, **28**, 622—623).—Fumarine is soluble in 11·2 parts of chloroform and in 78·68 parts of benzene, but is only very sparingly soluble in water, alcohol, ether, and petroleum. When treated with Fröhde's reagent, it first turns violet, then dark-green; with vanadyl sulphate, it gives an emerald-green colour which, after some hours, becomes yellowish-green; with sulphuric acid and sugar, it gives a dirty-violet coloration; with selenosulphuric acid, a pure violet. It is not coloured by chlorine-water, but becomes violet-brown with bromine-water and sulphuric acid. A crystal of potassium nitrate thrown into its solution in sulphuric acid colours the liquid, as it dissolves, first green, then violet, and lastly yellow. Potassium dichromate added to a fumarine salt throws down fumarine chromate; on adding concentrated sulphuric acid, intense green and violet streaks are produced, passing, after a few minutes, into green. M. J. S.

Preparation and Properties of Albumin, free from Ash. By E. HARNACK (*Ber.*, **22**, 3046—3052; compare Abstr., 1882, 747).—Albumin, free from ash, can be obtained as follows:—The copper-compound of albumin, prepared as previously described (*loc. cit.*), is purified by dissolving it in very dilute soda, reprecipitating with acetic acid, and washing well with water, the process being repeated several times; the precipitate is then dissolved in a considerable quantity of soda, the solution kept for 24 hours, the albumin precipitated by neutralising with hydrochloric acid, washed with water, and dried at 100°.

It is thus obtained in the form of a gelatinous, transparent, brittle, yellowish-red mass which is almost free from ash, 1 gram leaving a residue of about 1 milligram on ignition. It is free from phosphorus and phosphates, and iron could not be detected. When the moist substance is treated with pure, cold water, it gradually swells up and dissolves; the solvent action being hastened considerably by boiling. The dry substance shows a like behaviour, but it dissolves much more slowly. The residue obtained on evaporating the aqueous solution to dryness seems to have the same properties as the original substance.

Albumin, free from ash, is precipitated from its aqueous solution by acids, the precipitate being insoluble in excess; also by neutral salts, for example, sodium chloride, but the precipitate dissolves again if the solution is diluted very considerably. The precipitated albumin has the same properties as the original substance, but if the precipitate is boiled with the solution, it is gradually converted into a modification insoluble in water.

Albumin, free from ash, is precipitated from its aqueous solution by salts of the heavy metals, phosphomolybdic acid, potassium ferrocyanide, &c.; but it is not precipitated by alcohol, ether, phenol, or tannic acid. F. S. K.

Heat Coagulation of certain Proteïds. By J. B. HAYCRAFT and C. W. DUGGAN (*Brit. Med. J.*, 1890, i, 167—169).—It is found that there are various circumstances that affect the temperature at

which any proteïd enters into the condition of a heat-coagulum. If a solution of a coagulable proteïd is heated quickly, the proteïd will be found to coagulate at a higher temperature than if the heat is applied more slowly. The coagulation point is considerably raised by diluting the solution, and a very dilute solution may not coagulate even on boiling. The presence of certain neutral salts lowers, of others raises the coagulation temperature. The presence of acids lowers, of alkalis raises the coagulation temperature. These facts were ascertained to be true for egg albumin, serum albumin, vitelleïn, and serum globulin.

Halliburton (*J. Physiol.*, **5**) and Corin and Berard (Abstr., 1889, 1075) attempted to separate proteïds by means of fractional heat coagulation. Without doubting the possibility of fractionating some proteïds, the result of the present experiments seems to cast a doubt on the method adopted, unless other differences be demonstrated to exist between the various proteïds thus separated. It is thus possible that serum albumin or egg albumin may be single proteïds, and the fact that various precipitates at different temperatures are obtainable can be explained in one of two ways: either that the heat when applied for a long time (in Corin and Berard's experiments for upwards of an hour) alters the character of the proteïd in solution so that its temperature of coagulation is heightened, or that the result is simply the effect of dilution; a solution of serum albumin is raised to 75°; a precipitate occurs, and is filtered off; that left in solution is now more diluted, hence its coagulation temperature is higher. W. D. H.

Precipitation of Albuminoïds from Urine. By — Boymond (*J. Pharm.* [5], **20**, 481—482).—In attempting to form a filter of talc (previously washed in hydrochloric acid and water) for the filtration of turbid urine, the whole of the globulin contained in the urine was found to be removed by the so-called neutral substance composing the filter; whether any sereïn (? serum-albumin) was removed has not yet been determined. Experiments were instituted with other neutral substances, and it was found that bismuth subnitrate completely removed both globulin and "sereïn." This research is still being prosecuted. J. T.

Hæmoglobin. By A. Jaquet (*Zeit. physiol. Chem.*, **14**, 289—296). —A sample of dog's hæmoglobin, prepared according to Zinoffsky's method (Abstr., 1886, 165), gave the following percentage composition, which may be compared with the results obtained previously with dog's hæmoglobin (Abstr., 1888, 731), and with Zinoffsky's analysis of horse's hæmoglobin, in the following table:—

	Hæmoglobin of dog.		
	Previous analysis.	Present analysis.	Of horse (Zinoffsky).
C......	53·91	54·57	51·15
H......	6·62	7·22	6·76
N......	15·98	16·38	17·94
S......	0·542	0·568	0·39
Fe	0·333	0·336	0·335
O......	22·62	20·93	23·43

The formula for dog's hæmoglobin deduced from this second analysis is $C_{758}H_{1203}N_{195}S_3FeO_{218}$.

An analysis of hen's hæmoglobin was also made; the percentage composition was C, 52·47; H, 7·19; N, 16·45; S, 0·8586; Fe, 0·3353; O, 22·5; P, 0·1973.

The relation of S : Fe = 9 : 2; the relation of Fe : P = 1 : 1. The only other preparation of birds' blood that has been analysed is that of goose's blood by Hoppe-Seyler. He also found phosphorus present (0·77 per cent.), and this has generally been regarded as due to admixture with nucleïn; the relation of phosphorus to iron in the present research seems to indicate that the phosphorus may be actually in the hæmoglobin-molecule. W. D. H.

Physiological Chemistry.

Respiration of Entozoïc Worms. By G. Bunge (*Zeit. physiol. Chem.*, **14**, 318—324).—In an earlier communication (*ibid.*, **8**, 48) it was shown that the *Ascaris mystax*, the worm that lives in the intestine of the cat, will live four or five days in media quite free from oxygen.

Renewed experiments with *Ascaris acus*, from the intestines of the pike, are confirmatory of the above; these worms live for four to six days, and exhibit movements, in media free from oxygen. In the ultimate respiratory processes of these animals there must be a formation of energetic reducing substances (nascent hydrogen and easily oxidisable organic matter) which unite with one atom of the oxygen-molecule, even to a greater extent than in animals which breathe oxygen. These animals possess no respiratory apparatus.

In order to investigate this question more fully, larger varieties of *Ascaris* were employed. The *A. megalocephala* of the horse was found unsuitable, as it only lived for two days after removal from the intestine; the *A. lumbricoïdes* of the pig was therefore used; this lived from five to seven days. In boiled salt solution it gave off abundance of gas, which was collected over mercury, and was completely absorbed by potash, consisting of pure carbonic anhydride, and containing no hydrogen. The quantity of gas obtained in this time was from 5 c.c. to 10 c.c. per gram of the animal's body-weight. In three experiments, a small, measured quantity of oxygen was added to this gas artificially, but there was no diminution in its volume after the admixture; thus not only hydrogen, but other reducing substances are absent also. W. D. H.

Heat developed by the Action of Oxygen on the Blood. By Berthelot (*Compt. rend.*, **109**, 776—781).—The experiments were made with defibrinated fresh sheep's blood which had been allowed to remain in a closed flask for 24 hours. The scarlet colour had changed to purple, the sp. gr. was 1·057 at 9°, and the specific heat 0·872. It

was placed in the calorimeter, and a current of nitrogen, saturated with moisture, was passed through for some time. Dry oxygen was then passed in, and the temperature observed at frequent intervals. Before weighing the calorimetric vessel, the oxygen in the empty space was expelled by means of nitrogen.

In one experiment, 100 vols. of blood absorbed 20·2 vols. of oxygen, in another, 18·5 vols. The heat developed per 32 grams of oxygen was 14·63 Cals. in the first case and 14·91 in the second, or a mean of +14·77 Cals. The formation of silver oxide develops +14·0 Cals.; of barium peroxide, +24·2 Cals.; of lead peroxide, +24·5 Cals. per 32 grams of oxygen; and it is evident that the heat liberated by the formation of oxyhæmoglobin is of the same order of magnitude as the heat of formation of many true oxides.

The combination of carbonic oxide with hæmoglobin developed +18·0 Cals. and +19·4 Cals., or a mean of +18·7 Cals. per 28 grams, a disturbance of the same order of magnitude as the heat of formation of oxyhæmoglobin, but distinctly higher.

The heat developed by the action of oxygen on the blood is almost exactly one-seventh of the heat which would be liberated by the complete oxidation of carbon by the same quantity of oxygen, and hence it follows that of the total animal heat about one-seventh is developed in the lungs by the combination of oxygen with the blood, and the remaining six-sevenths in other parts of the body in consequence of oxidations and hydrations.

The development of heat in the lungs is almost exactly compensated by the absorption of heat due to the liberation of carbonic anhydride and water vapour, and whether the temperature of the blood in the lungs rises or falls is determined by the temperature of the inspired air, but the variation in one direction or the other is not greater than the tenth of a degree. C. H. B.

Animal Heat and the Heat of Formation and Combustion of Urea. By BERTHELOT and P. PETIT (*Compt. rend.*, **109**, 759—764). —See this vol., p. 206.

Artificial Digestion of Proteïds. By A. STUTZER (*Landw. Versuchs. Stat.*, **36**, 321—328).—The method proposed by the author consists in treating the food first with an acid pepsin solution and then with an alkaline pancreatic liquid, and determining the nitrogen in the undissolved substance; from the relation of the indigestible to the total proteïd nitrogen, the digestibility coefficient is calculated. The method gives, according to Pfeiffer (*Journ. f. Landw.*, **34**, 444), results nearly identical with those obtained by means of direct experiments with animals.

The pepsin solution is prepared by cutting the mucous skin of a fresh pig's stomach into small pieces and keeping it for one or two days with 5 litres of water, 100 c.c. of hydrochloric acid (containing 10 grams of hydrogen chloride) and 2·5 grams of salicylic acid; it is then poured through a flannel bag and filtered, first through a coarse and then through a dense filter paper. It is best to prepare several extracts at once.

The pancreas extract is obtained by cutting up the pancreas (1000 grams) of a bullock, rubbing it up with sand, and exposing it to air for 24—36 hours. It is then treated with lime-water (300 c.c.), glycerol (sp. gr., 1·23; 1 litre), and some chloroform, kept for four to six days, filtered, heated for two hours at 37—40°, and again filtered, if necessary. Before using the extract, 250 c.c. of it is mixed with sodium carbonate solution (750 c.c. containing 5 grams of the anhydrous salt), heated at 37 to 40° for one or two hours, and filtered.

The determination of digestible substance is made as follows:—the finely powdered food (2 grams) is tied up in paper and extracted with ether from five to six hours to remove the fat. It is then treated with the pepsin solution (250 c.c.) and heated at 37 to 40° for 24 hours, 10 per cent. hydrochloric acid (2·5 c.c.) being added at intervals of about one hour until the solution contains 1 per cent. of acid. It is then filtered through asbestos. The substance, with the asbestos, is heated with the alkaline pancreas extract (100 c.c.) for six hours at 37—40°, the liquid being stirred sometimes. After this it is filtered, washed with water, dried, and the nitrogen determined in the substance.

It was found that if the substance is treated with 400 c.c. of pepsin solution containing 0·2 per cent. of hydrogen chloride, without subsequent digestion with pancreas, somewhat less nitrogen is dissolved than when the less amount of more strongly acid pepsin is employed. But if the food is afterwards digested with pancreas, the final result is the same in both cases. N. H. M.

Absorption of Sugar from the Small Intestine. By S. GINSBERG (*Pfluger's Archiv*, **44**, 306—318).—v. Mering (*Arch. Anat. physiol., physiol. Abth.*, 1877, 379) showed that the chyle from the thoracic duct of the dog contained no more sugar during the digestion of carbohydrate than at other times, but that the percentage of sugar in the portal blood was increased under these circumstances.

Heidenhain pointed out (*Pflüger's Archiv. Supp.*, 1888, 71) that this is probably due to the fact that the water and substances, like sugar, easily soluble in water are taken up by the blood-vessels as they lie immediately beneath the epithelium, and so do not reach the more centrally situated lacteals of the villi. The present research, undertaken under Heidenhain's superintendence, was directed to ascertaining, whether by greatly increasing the amount of sugar and water in the food, some might not be found even in the chyle.

The first experiments were performed on rabbits, with results given in the following table (p. 277).

These show that during a normal diet the amount of sugar in both blood and chyle is very constant. The seemingly higher percentage in the latter is due to the fact that the percentage is taken for the total blood, including corpuscles. In round numbers 100 parts of blood contain 60 volumes of plasma; hence, the percentage in the plasma would average 0·28, which is higher than that in the chyle. The rise of the percentage during sugar feeding, both in blood and chyle, is very marked.

	Percentage of sugar in		Food.
	Blood.	Chyle.	
1	—	0·25	Normal diet.
2	0·18	0·23	„
3	0·18	0·25	„
4	0·18	0·23	„
Mean	0·18	0·24	„
5	0·22	0·36	5 grams sugar in 50 c.c. water.
6	0·39	0·76	15 „ 100 „
7	0·33	0·39	15 „ 100 „
8	0·31	0·46	25 „ 150 „
Mean	0·31	0·49	

The second series of experiments, made on dogs with a fistula of the thoracic duct, show the same result, and are still more satisfactory, as the same animal could be used in the two experiments.

The following table contains the results of a few of the experiments performed. The sugar solution was injected into the intestine.

	Percentage of sugar in				Amount injected.
	Blood.		Chyle.		
	Before injection.	After injection.	Before injection.	After injection.	
1	0·14	0·14	0·24	0·27	30 grams in 600 c.c. of water.
2	0·07	0·27	0·25	0·52	40 „ 400 „
3	0·09	0·18	0·22	0·35	20 „ 400 „
4	0·08	0·28	0·16	0·42	30 „ 400 „

W. D. H.

Osmosis with Living and Dead Membranes. By E. W. Reid (*Brit. Med. J.*, 1890, i, 165—167).—The process of diffusion of fluids through animal membranes is well known to be influenced by the vital condition of such membranes. (Cl. Bernard, Matteucci and Cima, &c.). In the present research the skin of the frog was chiefly employed; the liquids used were those which do not markedly impair the vitality of living tissues, such as physiological saline solution, or a 5 per cent. solution of glucose in this solution. The

osmometer used was either the ordinary Dutrochet instrument, or an oil-discharging osmometer in which the pressure was kept constant in order to avoid error from the occurrence of filtration. For recording purposes, advantage was taken of the photographic method in order to avoid friction; the height of the column of liquid being photographed on a very slowly revolving cylinder covered with sensitive paper. The following conclusions are drawn from the experiments:—(1.) The normal direction of easier osmotic transference of fluid through the living skin of the frog is in the direction from the outer towards the inner surface. (2.) The transference of fluid through the skin in the above direction is intimately associated with the physiological condition of its tissues. Conditions or agents tending to depress vitality diminish the transfer in the normal direction, while stimulants give rise to augmentation. (3.) The cause of the easier transfer of liquid from the outer towards the inner surface is probably to be found in the existence of an absorptive force dependent on protoplasmic activity, and comparable to the secretive force of a gland cell. (4.) In consequence of the absorptive force, acting from without inwards, an alteration of the relations of the surfaces of the skin to the two liquids used in an osmosis experiment modifies the rapidity of the transfer of liquid from one to the other side of the membrane, according as the force exerted by the living tissues is with or against the osmotic stream. W. D. H.

Effect of Feeding on the Secretion of Amidic Substances. By E. Schulze (*Bied. Centr.*, **18**, 733—734; from *Pflüger's Archiv*, **25**, 401—460).—The following are the results of the author's experiments:—(1.) The nearer the feeding of persons approaches to a pure animal diet, the greater is the amount of nitrogen as urea in proportion to the total nitrogen of the urine. (2.) The relation of uric acid to the total nitrogen decreases with meat diet as opposed to feeding with mixed food. This occurs in a still greater degree with a meat diet with use of abundance of alkaline water and absence of alcohol and narcotics, although the absolute amount of uric acid increases. (3.) The same holds good with regard to the relation of uric acid to urea. (4.) It is very probable that in fever, even in absence of respiratory derangement, there is not only an absolutely larger amount of uric acid produced, but also an increased proportion of uric acid relatively to total nitrogen and to urea. (5.) The use of plenty of alkaline water and the disuse of alcohol in treatment of gout are justified by experimental evidence which cannot be denied; these factors seem to be of greater importance than the prohibition of meat.

N. H. M.

Detection of Nitrous Acid in Saliva. By L. Ilosvay de N. Ilosva (*Bull. Soc. Chim.* [3], **2**, 388—391).—The saliva is boiled with an acetic acid solution of sulphanilic acid, the clear solution is decanted, and naphthylamine is added, when a rose coloration indicates the presence of nitrous acid, which is increased after a meal; the action of tobacco smoke retards the reaction considerably.

Nitrous acid could not be detected in the water moistening a cylinder

through which air had been respired; when, however, the respired air was passed through bulbs containing a 2 per cent. solution of sodium hydroxide for some time, an indication equal to that afforded by ordinary air under similar conditions was obtained, although from experiments made with the air of stables the authors conclude that respired air does contain more nitrous acid than ordinary air.

T. G. N.

Reducing Substances in Urine. By H. H. Ashdown (*Brit. Med. J.*, 1890, i, 169—172).—The most important substance that reduces an alkaline solution of copper oxide and that is apt therefore to be mistaken for sugar in urine, is glycuronic acid. It can only be identified with certainty by isolating it and examining its properties. A ready distinction, however, between sugar and this substance is that the addition of yeast to the former, even when dissolved in the urine, causes the occurrence of the alcoholic fermentation, and to the latter does not.

In man, the diagnosis of diabetes must in future be always more carefully made, as in one case, the first hitherto recorded, the reducing substance was found to be wholly glycuronic acid; the man in whom this occurred is in perfect health, and no symptoms of diabetes are present. If this state of things be shown to occur in other cases, the question becomes important in relation to life assurance.

In animals, the appearance of glycuronic acid in the urine is readily produced by the administration of certain drugs, camphor, phenol, &c.

In the present research, the following experiments were made:— The urine secreted after drugging with morphine contains, not sugar, but glycuronic acid; after the administration of chloroform, glycuronic acid, not sugar, is present. This confirms a previous investigation of Meyer. The so-called glycosuria of curare poisoning does not depend on the presence of sugar; there is no fermentation with yeast. The quantities of urine obtainable under these circumstances are, however, so small that it was not possible to separate out glycuronic acid. The administration of ether does not cause the appearance of any reducing substance in the urine. After section of the renal nerves, a paralytic secretion occurs; this contains a reducing substance, which was found to be glycuronic acid. W. D. H.

Nitrogenous Constituents of Dog's Urine. By L. Bleibtreu (*Pflüger's Archiv*, **44**, 512—535).—This investigation was carried out by the methods used by Böhland (Abstr., 1889, 536), and by Pflüger and Bleibtreu (this vol., p. 308). The results when the animal was fed on a meat diet are compared with those obtained when a mixed diet was used; they are given in the following table (p. 280); the numbers are percentages.

The urea thus increases in proportion when the diet is chiefly albuminous, and diminishes on a mixed diet. It is also seen that in filtrate II, that is, in the urine after the separation of "extractives"

	Total nitrogen (Kjeldahl).	Nitrogen in urea.	Nitrogen not in urea. Total N = 100.	Nitrogen in filtrate II after subtracting ammonia.	Nitrogen in filtrate II which is not present in the form of urea or ammonia. Total N in filtrate = 100.
Meat diet 1.	5·155	4·59	10·96	4·682	1·96
Meat diet 2.	5·14	4·931	4·07	5·0636	2·6
Mixed diet 3.	—	1 0155	—	1·061	4·3
Mixed diet 4.	0·721	0·61638	14·5	0·6841	9·9

by means of phosphotungstic acid, there is, in addition to urea and preformed ammonia, a nitrogenous substance which contains about 2 per cent. of the total nitrogen in this filtrate when the diet is albuminous, but rises to double or quadruple the amount when the diet is a mixed one. W. D. H.

Nitrogenous Constituents of Human Urine. By E. SCHULTZE (*Pflüger's Archiv*, **45**, 401—460).—This is a research carried out on the same lines as that in the preceding abstract. The investigation was carried out on the human subject, its object being to compare the variations in the amount of urea-nitrogen with the non-urea-nitrogen in relation to diet. The fullest details of analysis are given; the methods adopted were those of Pflüger and Bleibtreu. The conclusions arrived at are as follows:—

1. The urea-nitrogen increases in proportion to total nitrogen as the diet approaches a purely albuminous composition.

2. The uric acid increases absolutely, but diminishes relatively, both to total nitrogen and to the urea on a meat diet, especially if large quantities of alkaline water be taken and alcoholic drinks and narcotics be avoided.

3. Probably in fever the same relation of uric acid to total nitrogen and urea holds.

4. The use of abundant quantities of water and withdrawal of alcoholic beverages in cases of gout has thus a scientific basis.

W. D. H.

Action of related Chemical Compounds on Animals. By W. GIBBS and H. A. HARE (*Amer. Chem. J.*, **11**, 435—448).—This paper contains an account of the first part of a research having for its object a systematic study of the relation between the chemical constitution of compounds and their action on the animal organism. Dogs and frogs were experimented on, and a description is given of the action of the nitrophenols, the nitranilines, and the amido- and nitrobenzoic acids on these animals when administered by the stomach or hypodermically.

The nitrophenols cause death by paralysing the heart, and not by a respiratory action; the nervous system is unaffected by them, except that the vagus nerves are slightly stimulated by the ortho- and meta-compounds, but depressed by the para-compound. The lethal dose per kilo. of body weight is 0·1 gram of the ortho-, about 0·1 gram of the meta-, or 0·01 gram of the para-compound, when injected into the jugular vein. The nitranilines all act by stimulating the peripheral vagi, and so producing a very marked slowing of the pulse. In the case of the ortho-compound, the lethal dose is 0·3 gram per kilo.; methæmoglobin is produced in the blood, and the sensory side of the spinal cord is slightly affected, but this is probably caused indirectly by the changes in the blood. Given by the stomach it produces curious paroxysms of sneezing. The meta-compound has but a very feeble effect on the nerves, and this depends on the development of methæmoglobin in the blood, all the symptoms being those of aniline poisoning. The para-compound is the most poisonous, the lethal dose being 0·04 gram per kilo. of body weight when injected into the jugular vein. The amidobenzoic acids and the nitrobenzoic acids were found to be without effect on the animal organism.

C. F. B.

Is Potassium Ferrocyanide Poisonous? By P. CARLES (*J. Pharm.* [5], **20**, 486—489).—The evidence here collected from various sources leads to the conclusion that this salt is not poisonous.

J. T.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Yeast on the Bouquet of Wines. By A. ROMMIER (*Bull. Soc. Chim.* [3], **2**, 297—300).—Having previously shown that cultivated yeast determined the non-development of the cells occurring naturally on the grape when the former was added to juice in which the latter existed, the author fermented the juice of an inferior grape and of hothouse grapes respectively with yeast cultures obtained from the Champagne, Côte d'Or, and Buxy districts, and found that in each case the resulting wines had the bouquet of the wines from whence the yeasts were derived.

T. G. N.

Influence of Carbonic Anhydride on the Products of Fermentation. By L. LINDET (*Bull. Soc. Chim.* [3], **2**, 195).—The carbonic anhydride evolved during fermentation by means of yeast was not allowed to escape, but retained in the vessels under pressures of 20, 200, 430, and 600 mm. of mercury respectively, without affecting the amount of alcohol produced or the weight of yeast formed.

T. G. N.

Inverting Ferment. By O. KELLNER, Y. MORI, and M. NAGAOKA (*Zeit. physiol. Chem.*, **14**, 297—317).—Koji is the name of a substance used in China and Japan in the preparation of rice wine and

alcohol. It consists of the mycelium and spores of a fungus. When investigated, it was found to contain a powerful inverting ferment which changes cane sugar into dextrose and levulose, maltose into dextrose, and starch into dextrin, maltose, and dextrose; it probably does not alter lactose or inulin. The invertin of yeast acts on cane sugar only, and the name suggested for the ferment of Koji is *invertase*. Its action is much hindered by the presence of common salt, but it is not wholly destroyed even by 20 per cent. of that salt. W. D. H.

Nitrification of Ammonia. By T. SCHLOESING (*Compt. rend.*, **109**, 883—887).—Under normal conditions, nitrification of ammonia takes place without any loss of free nitrogen, but when a large excess of ammonium salt is present, there is a very distinct loss of nitrogen in this manner. This loss is due to the formation of a small quantity of nitrite, owing to absence of an excess of oxygen. The nitrite interacts with the ammonium salt, with production of free nitrogen; it also retards nitrification, and is itself but slowly oxidised.

It is possible that the free nitrogen is not the result of interaction between the nitrite and the ammonium salts, but is liberated as a result of limited oxidation of the ammonia; this point, however, can only be determined by further experiment. C. H. B.

Fermentation of Manure in Absence of Oxygen. By T. SCHLOESING (*Compt. rend.*, **109**, 835—840).—When fresh manure from cows is kept at 42° to 52° in an atmosphere of carbonic anhydride, it undergoes fermentation with evolution of hydrogen, methane, and carbonic anhydride, but no free nitrogen is evolved. Hydrogen is only liberated in the early stages of the change, and disappears from the gases as fermentation progresses. The ratio of methane to carbonic anhydride approaches unity only towards the end of the process, and varies irregularly throughout the fermentation.

No nitrogen is evolved at any stage, but the quantity of ammonia present increases. The quantity of oxygen and hydrogen in the evolved gases is greater than the quantity lost by the manure, and it is evident that the water which is present plays an active part in the fermentation, the oxygen combining with carbon to form carbonic anhydride, whilst the hydrogen is converted into methane.

C. H. B.

Formation of Cane Sugar in Etiolated Plant Shoots. By E. SCHULZE (*Chem. Centr.*, 1889, ii, 694—695; from *Ber. Deut. bot. Gesell.*, **7**, 280—281).—The etiolated shoots of *Lupinus luteus* were examined, by means of the method described by the author (compare Abstr., 1888, 624), for cane sugar, of which 30 grams (crystallised) was obtained from 800 grams of air-dry shoots, besides a considerable amount which must have been lost in the separation and purification. Before germination, not the least trace of sugar was detectable in the lupins. As is already known, starch is also formed during the process of germination of this seed in the absence of light, the other nitrogen-free substance which is present in the seeds as

reserve material disappearing as the formation of sugar and starch proceeds. J. W. L.

Living Vegetable Protoplasm. By T. BOKORNY (*Pflüger's Archiv*, **45**, 199—219).—The difficulty of applying chemical reagents to living structures in many cases consists in the fact that the reagent destroys the life of the material under investigation. Weak solutions of alkalis have not, however, this objection; they produce changes in the cells, but these are considered to be vital changes, that is, evidence of the living activity, and not of the death of the protoplasm.

These changes may be grouped together under the general term "aggregation." This term was first used by Darwin to express the change that occurs in the tentacles of *Drosera* on the application of weak solutions of ammonium carbonate; this consists in the collection of the protoplasm into separate particles. The term has since been extended to somewhat similar phenomena in other plants; De Vries (*Botan. Zeit.*, 1886, 1), however, limits it to the contraction of the vacuole wall, and does not speak of the formation of proteïd granules in the vacuole contents as aggregation. Pfeffer distinguishes between an outer and inner cell-membrane, the former lining the cell wall proper, the latter surrounding the vacuole fluid, and betweeen the two is what he terms granule-plasm (Körner-plasma), but which does not necessarily always contain granules.

In the present research, a large number of careful microscopic observations are recorded. The plants, the cells of which were examined were *Spirogyra*, *Drosera*, *Tulipa*, *Crocus*, *Cotyledon coccinea*, &c. The weak alkalis chiefly used were ammonia (1 : 5000) and caffeïne (1 : 1000). Weak potassium hydroxide, various amines, tetrethylammonium hydroxide, toluylenediamine, quinine, atropine, &c., were also used in some experiments.

The following cases of aggregation could be distinguished:—(1.) The whole protoplasm contracts equally; this is somewhat different from, but very similar to plasmolysis; it is seen in crocus papillæ. (2.) The vacuole wall (inner cell-membrane of Pfeffer) contracts alone, or to a much greater extent than the rest of the cytoplasm; this is well seen in the red epidermal cells of the petals of tulips and primulas. (3.) The "granule-plasm" collects into granules or discs; these are exceedingly minute from the action of ammonia on *Spirogyra* cells, but much larger from the action of solution of caffeïne on sections of the leaves of *Cotyledon coccinea* and *Echeveria gebbiflora*. (4.) The vacuole-fluid, that is, the cell-sap with active albumin either in solution or in a greatly swollen condition, becomes pervaded with larger or smallar granules; this is seen in *Drosera*, *Spirogyra*, and several other plants. W. D. H.

Vegetable Cell-membranes. By E. SCHULZE, E. STEIGER, and W. MAXWELL (*Zeit. physiol. Chem.*, **14**, 227—273; compare Abstr., 1889, 916).—This investigation shows that the membrane of vegetable cells contains in addition to cellulose several other carbohydrates which differ from it widely in their properties. They are all insoluble

in cuprammonium hydroxide, but differ in certain other reactions; by hydrolysis, however, they all yield pentaglucoses (arabinose, xylose, &c.); by warming with phloroglucinol and hydrochloric acid give a cherry-red colour; and by treatment with very dilute mineral acids differ from cellulose in being quickly converted into sugar; the varieties of sugar formed being galactose, mannose (seminose), and pentaglucoses. The term cellulose as used by Reiss (Abstr., 1889, 687) evidently includes these carbohydrates; it is, however, advisable to restrict the word cellulose to those constituents of the cell-wall which are but little affected by strongly diluted mineral acids, which are soluble in cuprammonium hydroxide, which further are coloured blue by chloride of zinc and iodine, or iodine and sulphuric acid, and which lastly are converted by strong sulphuric acid into dextrose. The term proposed for these other carbohydrates is that of "paragalactan-like substances." It appears doubtful as to whether cellulose is a single substance, but this was not specially investigated.

The paragalactan-like constituents of the cell-wall appear to be of some physiological importance; they seem to be more soluble than cellulose, and enter into solution during germination, functioning as a reserve material before that process commences. It is very doubtful if true cellulose acts in this way.

The nutritive value of these substances in the animal economy appears, like that of cellulose, to be small, as they are not digestible by the various digestive juices. On oxidation with nitric acid, they yield mucic acid. From the point of view of analyses of starch in vegetable substances, these paragalactan-like materials are of some importance, as they, like starch, pass into solution on treatment with dilute mineral acids. W. D. H.

Non-Nitrogenous Reserve Substance of the Seeds of Lupinus luteus. By E. SCHULZE and E. STEIGER (*Landw. Versuchs.-Stat.*, **36**, 391—478).—The ethereal extract of the seeds of *Lupinus luteus* contained:—Glycerides, fatty acids, and wax 5·99, cholesterin 0·15, and lecithin 0·17 per cent. in the dry matter of the seed (freed from the shells). A further amount of lecithin can be extracted from the seed by alcohol, making a total of 2·10 per cent. (in dry seed). After being allowed to germinate for 14 days, 78·7 parts of dry matter remained and yielded an ethereal extract containing:—Glycerides, &c., 1·50 part, cholesterin 0·25 part, and only a trace of lecithin. The amount of lecithin extracted by alcohol was 0·44 part.

β-Galactan (Steiger, Abstr., 1886, 608) is a white, amorphous powder, consisting of microscopic globules. The aqueous solution is not coloured by iodine, and only reduces Fehling's solution when it has been heated with an acid. New determinations of rotatory power gave the mean:—$[\alpha]_D = +148·6°$. When β-galactan (100 parts) is heated with nitric acid, mucic acid (41·16 parts) is formed. The acetyl-derivative is a white powder melting at 101—102°. The amount of β-galactan contained in the dry seeds (without shells) was determined indirectly (1) as glucose, (2) as mucic acid. The first method gave in different samples:—(*a*) 10·20, (*b*) 10·02, (*c*) 9·48 and (*d*) 6·36 per cent.; the second method gave in sample (*a*) 8·5

and in (*e*) 7·65 per cent. With regard to the first method, it is shown that the seeds contain no cane-sugar which would affect the results.

Paragalactan (paragalactin, Abstract, 1887, 460), $C_6H_{10}O_5$ (?), could not be obtained free from cellulose. It dissolves partly in water when heated under a pressure of 1½ or 2 atmospheres; the filtered solution, when heated with hydrochloric acid, reduces Fehling's solution, and the residue obtained by evaporating the solution yields mucic acid when oxidised by nitric acid. It is not soluble in diastase solution. When heated with phloroglucinol and hydrochloric acid, a cherry colour is produced. 5 per cent. aqueous potash dissolves it partly; a salt seems to be formed.

Paragalactan is contained not only in the cotyledons, but also in the seed-shell. A carbohydrate probably identical with paragalactan was found in the seeds of *Soja hispida*, *Pisum sativum*, and *Faba vulgaris*.

When lupin seeds are allowed to germinate in the dark for six days, all the β-galactan is used up, whilst a great part of the paragalactan dissolves; glucose (not galactose), cane-sugar, and cellulose are formed. N. H. M.

Carrotene in Leaves. By ARNAUD (*Compt. rend.*, **109**, 911—914).—The proportion of carrotene in leaves varies with the species of the plant, but oscillates between 0·1 and 0·2 per cent. of the dried leaf. It varies with the age of the plant, is at a maximum during inflorescence, and then gradually diminishes, but never entirely disappears. Its quantity is affected by light, and, like chlorophyll, it tends to disappear in the dark.

Carrotene can absorb 24 per cent. of its weight of oxygen, but remains unaltered in the living leaf, and very probably undergoes alternate oxidation and reduction in such a manner that its quantity remains almost constant for short intervals of time. It is highly probable that carrotene is of very great physiological importance. C. H. B.

Mussœnda Coffee. By W. R. DUNSTAN (*Pharm. J. Trans.* [3], **20**, 381).—It has been asserted by Lapeyrère, that the seeds of a plant which he considers to be a new species of *Mussœnda*, and calls *Mussœnda borbonica*, may be employed as a substitute for coffee. The plant grows in the island of Réunion, and its seeds are said to contain 0·3—0·5 per cent. of caffeïne. An examination of the plant at Kew showed that it is not a *Mussœnda*, but *Gærtnera vaginata*, which belongs to the natural order *Loganiaceæ*. The author found that the seeds contained neither caffeïne nor theobromine; strychnine and brucine were also absent, and the only alkaloïd that could be detected was a trace of choline. W. R. D.

Wine Statistics of Germany. (*Zeit. anal. Chem.*, **28**, 525—580).—The analyses of wines and musts here given, in continuation of those published in *Zeit. anal. Chem.*, **27**, 729, *et seq.*, include numerous brands from the wine districts of Rhein-Hesse, Rheingau, Rhine Palatinate, Baden, Würtemberg, Lower Franconia, Alsace, and Lorraine, and of vintages from 1884 to 1888. M. J. S.

Experiments on Ensilage conducted at Crawley Mill Farm, Woburn, 1884-87. By J. A. VOELCKER (*Journ. Roy. Agr. Soc.* [2], **22**, 483—513, and **23**, 403—417).—The object of the experiments was to determine the relative feeding values of silage as compared with roots and hay-chaff. The method employed was to feed four bullocks with weighed amounts of hay-chaff and swedes, and four more with an amount of silage containing the same quantities of dry matter, woody-fibre, and nitrogen as the hay-chaff and swedes contained; all the animals had, besides, weighed amounts of decorticated cotton-cake and maize-meal. In the first year's experiments, grass silage of inferior quality and clover silage which was of thoroughly good quality were employed. In both cases a much greater increase was obtained with roots and hay-chaff than with silage.

In the second year the following series of experiments were made:—(1) sour silage against roots and hay-chaff; (2) sweet silage against roots and hay-chaff; (3) oat silage against roots and straw-chaff; (4) oat silage against hay. This time the grass employed was of very fair quality. The bullocks fattened well on both sour and sweet grass silage of good quality, but still not so well as with roots and hay-chaff; whilst oat silage proved, in this instance, to be superior to either straw-chaff with roots or to hay. It was found that the oat silage when well made keeps perfectly for at least two years. The following table shows the percentage of nitrogen, albuminoïd nitrogen, and non-albuminoïd nitrogen in the silage:—

	In fresh.			In dry.		
	Albuminoïd nitrogen.	Non-albuminoïd nitrogen.	Total nitrogen.	Albuminoïd nitrogen.	Non-albuminoïd nitrogen.	Total nitrogen.
Sweet silage (grass)..	0·45	0·22	0·67	1·27	0·62	1·89
Sour silage (grass....	0·28	0·23	0·51	1·03	0·85	1·88
Oat silage	0·15	0·15	0·30	0·64	0·64	1·28
Hay.......................	1·37	0·37	1·74	1·58	0·43	2·01

The object of the third year's experiments was to determine the value of grass made into hay as against that of the same grass converted into silage. The grass employed was of very fair quality, and the silage was extremely good and well made.

The percentage of nitrogen, albuminoïd nitrogen, and non-albuminoïd nitrogen in the grass, and in the hay and silage prepared from it, was as follows:—

	In fresh.			In dry.		
	Albuminoïd nitrogen.	Non-albuminoïd nitrogen.	Total nitrogen.	Albuminoïd nitrogen.	Non-albuminoïd nitrogen.	Total nitrogen.
Grass	0·34	0·08	0·42	1·29	0·30	1·59
Hay.......................	1·16	0·19	1·35	1·41	0·23	1·64
Silage (sour)...........	0·24	0·27	0·51	0·87	0·98	1·85

100 parts of grass gave:—Good silage 87·15 parts, inferior and mouldy silage 4·56 parts, loss by fermentation, &c., 7·29 parts. The produce in hay was:—good hay 29·77 parts, inferior hay 2·61 parts, water and loss 67·62 parts.

The experiments show that the silage from 28,995 lbs. of grass (the produce of 2·4 acres) and the hay from 34,442 lbs. of grass (the produce of 2·8 acres) gave equal feeding results.

The results of similar experiments made at Wilmington, near Shrewsbury, showed a slightly larger gain with silage than with hay prepared from the same grass. N. H. M.

Ammonia and the Nutrition of Plants. By A. Müntz (*J. Pharm.* [5], **20**, 489—492).—Experiments were made to ascertain whether salts of ammonia could be utilised by the roots of plants without first being converted into nitrate. Seeds of bean, horse-bean, maize, barley, and hemp were freed from nitrification germs, and sown in soil freed from nitrates and germs, and placed in glazed boxes supplied with sterilised air. Ammonia in the form of sulphate was supplied. A similar set of pots was prepared containing germs of the nitric ferment. The sterilised soil contained no nitrates either at the beginning or end of the experiment; the non-sterilised soil contained no nitrates at beginning, but yielded 91·2 and 420·0 milligrams per kilo. at the end of the trial. In the sterilised pots, the plants grew well, and assimilated all the nitrogen required from the ammonium salt, showing that nitrification is not essential.

J. T.

Effect of Manuring with Ammonium Sulphate and with Sodium Nitrate. By M. Maercker (*Bied. Centr.*, **18**, 724—729).—In order to determine the effect of calcium carbonate on the manurial action of ammonium sulphate, six plots of land, supplied with phosphoric acid, or kainite, received the following:—(*a*) Nothing; (*c*) ammonium sulphate (87 to 130 lbs. per acre); (*e*) twice the amount of ammonium sulphate supplied to *c*. *b*, *d*, and *f* were treated in the same way as *a*, *c*, and *e* respectively, except that calcium carbonate (15·6 cwt. per acre) was added. The crops grown were: oats, barley, winter wheat, beetroot, mangel-wurzel, and potatoes. The plots with the larger amounts of nitrogen gave much more produce than the others, and the addition of calcium carbonate was beneficial in every case, with the exception of the beetroot, which had no ammonia.

Experiments were also made on the comparative manurial values of ammonium sulphate and sodium nitrate on barley, oats, potatoes, and beetroot. When smaller amounts of the two manures were used, the same increase of crop was obtained in all cases. The same holds good for corn crops when greater amounts of the manures were applied; whilst in the case of the root crops, a heavy manuring with sodium nitrate was found to be superior to an equal amount of nitrogen in the form of ammonia. N. H. M.

Amount of Mineral Matter and the Manurial Value of the Cupules of the Beech from Different Soils. By R. Hornberger

(*Landw. Versuchs-Stat.*, **36**, 329—335).—The beech cupules which were examined were from trees grown on two different soils, the Buntsandstein and the Muschelkalk. The cupules from the Muschelkalk are generally the larger and stronger, 1000 containing 614·4 grams of dry substance, whilst 1000 cupules from the Buntsandstein yield only 500·5 grams of dry matter. The following are the analytical results :—

	Pure ash p. c. in dry.	Nitrogen p. c. in dry.
I. Cupules from Buntsandstein....	2·582	0·330
II. ,, ,, Muschelkalk	1·825	0·379

The pure ash contains, per cent. :—

	K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3.	Mn_3O_4.	P_2O_5.	SO_3.	SiO_2.
I.	32·09	2·26	8·44	3·38	7·84	3·22	5·05	1·63	34·42
II.	38·87	1·83	29·04	3 59	4·44	1·21	7·29	4·56	10·21

The manurial value of the cupules differs very little for the two kinds, and is relatively small, owing to the low percentage of nitrogen.

The following analyses show the percentage composition of the dry matter of (1) the shells; (2) the seeds; and (3) the whole beech-nuts from trees grown in the Buntsandstein. 1000 of the beech-nuts contained 159·86 grams of dry matter, 105·82 grams of which belonged to the seeds, and 54·04 grams to the shells.

	Pure ash.	Nitrogen.
1. Shells	1·5160	0·4930
2. Seeds	3·9900	3·9400
3. Whole beech-nuts.....	3·1536	2·7747

The pure ash contained, per cent. :—

	K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3.	Mn_3O_4.	P_2O_5.	SO_3.	SiO_2.
1.	2·744	0·462	6·949	1·092	0·344	1·475	0·572	0·467	0·865
2.	14·597	0·243	4·301	4·180	0·320	1·824	11·291	2·221	0·159
3.	10·590	0·317	5·196	3·136	0·328	1·706	7·668	1·628	0·397

N. H. M.

Analytical Chemistry.

Bottle for Washing and Absorbing Gases. By F. A. KÜHNLENZ (*Zeit. anal. Chem.*, **28**, 608).—The gas bubbles passing through the liquid are caught by a series of glass bells, each of which has a short, straight tube through it to carry off the unabsorbed gas as soon as the bell becomes full, and these tubes are alternately on opposite sides of the bells, so as to retard the exit of the gas as much as possible.

M. J. S.

Detection of Free Chlorine in Hydrochloric Acid. By KUPFFERSCHLAEGER (*Bull. Soc. Chim.* [3], **2**, 134—136).—Pure concentrated hydrochloric acid diluted with one-fourth its volume of water does not attack granulated copper until heated at 200°, but slight traces of chlorine determine the solution of the metal in the cold, with consequent coloration of the acid.

Although pure hydrochloric acid has no action on phosphorus, in the presence of free chlorine an action obtains, and the solution produced gives a coloration and precipitate with ammonium molybdate.

T. G. N.

Action of Sulphuric Acid on the Haloid Salts of the Alkalis in Presence of some Metallic Salts. By D. VITALI (*Chem. Centr.*, 1889, ii, 398—399; from *L'Orosi*, **12**, 225—229).—Although concentrated sulphuric acid liberates the halogen acids from their alkaline salts when salts of the heavy metals are absent, this does not always take place if certain of the latter are present. If, for instance, sulphuric acid is added to a chloride in presence of an excess of cupric sulphate, anhydrous cupric chloride is precipitated.

The study of several reactions of this nature has led the author to recommend them as a means of distinguishing between chlorides, bromides, and iodides of the alkalis. If a little of a solution containing a chloride or bromide is evaporated to dryness, and one or two drops of concentrated sulphuric acid containing cupric sulphate in solution added, a yellow coloration is indicative of the presence of a chloride, whereas bromides cause a deep violet coloration; both colours are discharged on adding water. In the case of an iodide, iodine is liberated, and if cupric sulphate is present, the mixture becomes black, and *cuprous* iodide is formed, which remains as a white precipitate on adding water. The liberated iodine may be separated by shaking with chloroform. These latter reactions serve to distinguish iodides from bromides. If after adding a sulphuric acid solution of cupric sulphate to a bromide the mixture is shaken with ether, the latter becomes grass-green. Nickel salts alone cause a yellow coloration with sulphuric acid, which is not altered in presence of chlorides or bromides, but iodides cause a brown coloration with nickel sulphate and sulphuric acid; the solution contains free iodine, but no precipitate.

Both ferric and ferrous salts cause a beautiful, blood-red coloration with alkaline bromides and strong sulphuric acid; this disappears on addition of water.

Gold salts produce a cherry-red coloration under these circumstances, changing to yellow on addition of water.

Cobalt salts dissolve in concentrated sulphuric acid with a violet coloration, which changes to peach colour on addition of bromides, whilst chlorides cause a passing blue coloration at the junction of the liquids, the whole becoming peach-coloured on shaking.

J. W. L.

Estimation of Sulphur in Organic Compounds. By W. M. BURTON (*Amer. Chem. J.*, **11**, 472—474).—A modification of Sauer's method (compare this Journal, 1873, 939). The substance to be

examined is burned in a combustion tube arranged in the manner recommended by Sauer, and the products of combustion are collected in excess of a standard solution of potash; the excess of potash is ascertained by titration with standard sulphuric acid, the indicator used being tropæolin OO, which is not sensitive to carbonic anhydride, or to alkaline sulphites. The sulphuric acid solution contained 0·015312 gram per 1 c.c., and the potash solution was roughly equivalent to this; accurate results were obtained.

The amount of potash neutralised by the sulphurous anhydride evolved during the combustion is a measure of the sulphur in the substance examined. A slightly diminished pressure is maintained in the tube during the experiment, and at its conclusion any gases left are swept out by a current of air or oxygen. A figure of the apparatus is given in the paper. It is evident that this method cannot be used in the case of compounds containing phosphorus, arsenic, or any of the halogens. C. F. B.

Simultaneous Estimation of Sulphur and Carbon. By L. PRUNIER (*Compt. rend.*, **109**, 904—906).—The substance is mixed with 80 to 100 times its weight of pure crystallised potassium permanganate, and the combustion is conducted as with cupric oxide. The evolved gas is passed through a solution of potassium permanganate; all the sulphur and carbon remain in this solution, or in the combustion tube. The contents of the tube are treated with water and filtered through asbestos; all the sulphur passes into solution. Half the filtrate is heated with hydrochloric acid, and the sulphur precipitated as barium sulphate in the usual way. The remainder is boiled for a long time with sulphuric acid, care being taken that excess of permanganate is present, and the evolved carbonic anhydride is absorbed in the usual way. Any carbon in the insoluble portion is oxidised in a similar manner. The permanganate must be free from nitrates, chlorates, and other substances which would interfere with the estimation of the carbon. C. H. B.

Titration of Small Quantities of Gases in Mixtures. By P. BEHREND and H. KAST (*Dingl. polyt. J.*, **270**, 423—435).—The authors have examined Bunte's process for estimating volumetrically small quantities of gases in mixtures by means of Bunte's gas burette. The volume of gas employed is only about 100 c.c. The method is applicable to the estimation of hydrogen sulphide, ozone, and sulphurous anhydride. For the determination of hydrogen sulphide, a solution of iodine is used which contains 1·134 grams of iodine in 1 litre, so that 1 c.c. = 0·1 c.c. of hydrogen sulphide. 100 c.c. of the gaseous mixture is measured off into the burette, the remainder of the water in the measuring tube then run out to the lower mark of the same, and iodine solution added gradually, with constant shaking, until the mixture assumes a yellow tint. The turbidity formed owing to the separation of sulphur assists in determining the end of the reaction, which may be still further aided by introducing a few drops of thin starch paste, previously treated with sodium hydrogen carbonate;

into the burette. The authors have employed this method for the determination of hydrogen sulphide in a mixture of this gas with coal gas, the results being checked gravimetrically by passing a weighed volume of the gas through an acetic acid solution of lead acetate and again weighing. The results, which are tabulated in the paper, show a mean difference of 0·04 per cent. between the two methods. The process has also been used in order to ascertain the rate of formation of hydrogen sulphide at various stages during the carbonisation of coal, the samples of gas being taken from the ascension pipes. The coals employed were: Bohemian lignite, Saar coal, and Tyne Boghead Cannel. The results show that the first two kinds of coal give off the maximum amount of hydrogen sulphide immediately after the retorts have been charged, whilst in the case of the English coal, the maximum formation of gas takes place 35 minutes after charging.

In order to determine ozone in oxygen containing this gas, a measured volume (90 or 100 c.c.) is treated in the gas burette with an excess of potassium iodide solution (about 7 grams of a solution containing 17 grams of iodide in 100 c.c.) and dilute sulphuric acid. The iodine thus separated is then titrated with standard sodium thiosulphate, and from the quantity of iodine found that of the ozone is calculated. D. B.

Action of Sulphides on Chloral and Chloroform. By PRUNIER (*J. Pharm.* [5], **20**, 385—390).—The author deals with the reactions involved in Baudrimont's proposed application of chloral for the detection of alkaline sulphides and hydrosulphides. In aqueous solution, the monosulphide gives a brownish-red coloration or precipitate, whilst the hydrosulphide gives a white precipitate. It is necessary that the chloral should be in excess, and the solution should remain slightly acid or at least neutral to litmus, the condition which obtains when the sulphide is added to excess of chloral. J. T.

Estimation of Nitrogen in Ammonium Magnesium Phosphate. By P. MAISSEN and E. ROSSI (*Chem. Cent.*, 1889, ii, 611—612, from *l'Agric. pratica*, **3**, 430—432).—A specimen of this salt contained 5·40 per cent. of nitrogen as determined by Dumas' method. When distilled, however, with excess of magnesia in water, only 4·113 to 4·598 per cent. of nitrogen could be obtained, or by protracted distillation up to 4·772 per cent., and finally, when the distillation was proceeded with, until Nessler's reagent showed the absence of ammonia in the distillate, up to 5·25 per cent. of nitrogen was found to pass over. If, on the other hand, the phosphate is dissolved in hydrochloric acid and the solution neutralised with magnesia, 5·382 to 5·412 per cent. of nitrogen passed over with the first two-thirds of the liquid. Boussingault has drawn attention to this stability of the ammonium magnesium phosphate when boiled with excess of magnesia; and, since in the estimation of ready formed ammonia in manures this becomes of importance, the author recommends that such substances should be first acidified with hydrochloric acid and then rendered alkaline with magnesia. J. W. L.

Jodlbauer's Modification of Kjeldahl's Method for the Estimation of Nitrogen in Nitrates. By A. DEVARDA (*Chem. Zeit.*, 13, 388—389).—With regard to the Jodlbauer method, it is pointed out:—1. That it is very good for the estimation of the total nitrogen in manures, but for nitrate manures, even when all precautions are taken, it cannot compare with the author's evaporation method as regards accuracy and simplicity; 2. That the use of a mixture of sulphuric acid, phenol, and phosphoric acid instead of phenol and sulphuric acid, is not altogether an advantage; 3. That with 0·5 gram of a nitrate the results are no better with than without cooling, but in the presence of much organic matter, cooling is advisable during nitration; 4. That by adding sulphuric acid at the same time as the phenol-sulphuric acid rather lower results are obtained than by adding the sulphuric acid subsequent to the nitration with phenol-sulphuric acid.

D. A. L.

Detection of Nitrous Acid in Saliva. By L. ILOSVAY DE N. ILOSVA (*Bull. Soc. Chim.* [3], **2**, 388—391).—See this vol. p. 278.

Quantity of Nitric Oxide produced in the Combustion of Nitrogenous Organic Compounds with Copper Oxide. By F. KLINGEMANN (*Ber.*, **22**, 3064—3069).—The author has made a large number of experiments with the object of ascertaining the quantity of nitric oxide which is produced in the combustion of nitrogenous organic compounds with copper oxide.

Frankland and Armstrong's method for determining nitrogen (and nitric oxide) was employed (compare this Journal, 1868, 109).

The results, which are given in tables, show that the quantity of nitric oxide produced is independent of the relative quantity of nitrogen in the compound; hydrazine-derivatives, for example, although containing a large proportion of nitrogen give little or no (generally 0 to 1·0 per cent.) nitric oxide, whilst azines and glyoxalines, in spite of the small proportion of nitrogen which they contain, yield very considerable quantities (generally 5 to 10 per cent.) of nitric oxide. Nitro-compounds give very variable (from 0 to 5 per cent.) quantities of nitric oxide; picric acid yields 6 per cent.

F. S. K.

Estimation of Phosphoric Acid in Slags. Formation of Tetrahydrated Ferric Phosphate. By G. ARTH (*Bull. Soc. Chim.* [3], **2**, 324—327).—In eliminating by means of nitric acid the residual hydrochloric acid from slag, which had been treated with the latter reagent to remove silica, a probable source of error is described by the author, insomuch as a tetrahydrated ferric phosphate, $Fe_2(PO_4)_2 + 4H_2O$, is precipitated as a yellow, granular powder. This differs from the normal ferric phosphate resulting from the precipitation of a ferric salt by disodium phosphate in not suffering dehydration at 110°. It may be artificially produced by evaporating a solution of ferric chloride (4 mols.) and disodium phosphate (1 mol.) with an excess of nitric acid; as the solution becomes syrupy, an abundant separation of this phosphate occurs.

T. G. N.

Analysis of Natural Phosphates. By H. LASNE (*Bull. Soc. Chim.* [3], **2**, 313—324).—The author states that all natural phosphates contain calcium fluorophosphate, CaF_2,Ca_3PO_4, and describes at length his method for estimating all the constituents of these minerals. T. G. N.

Estimation of Hypophosphites. By F. MOERK (*Chem. Centr.*, 1889, ii, 553; from *Amer. J. Pharm.*, **61**, 326).—The solution of sodium hypophosphite is oxidised with bromine (4 mols. of hydrogen bromide being formed by the oxidation of each molecule of hypophosphite). The solution is boiled to expel the excess of bromine, and excess of calcium chloride is added, each molecule of sodium dihydrogen phosphate liberating two molecules of hydrogen chloride. The solution is finally titrated with alkali, phenolphthaleïn being used as indicator; each molecule of hypophosphite being equivalent to 6 mols. of potassium hydroxide. It is to be noted that the author does not take into account the loss of hydrogen bromide which would occur when boiling off the bromine. J. W. L.

Detection and Estimation of Alkaline Hydroxides in Presence of Alkaline Carbonates. By L. DOBBIN (*J. Soc. Chem. Ind.*, **7**, 829—830).—This method is based on the fact that a solution of potassium mercuric iodide mixed with even a large quantity of a solution of potassium or sodium carbonate remains quite colourless on the addition of ammonium chloride, whilst an abundant brown precipitate is produced on the addition to this mixture of a few drops of alkaline hydroxide solution. For use as a qualitative test for alkaline hydroxide, a very delicate reagent is prepared in a short time by taking a small quantity of a solution of mercuric chloride, adding potassium iodide until the red precipitate just redissolves, and then adding a drop of ammonium chloride solution; whilst for quantitative estimation a standard ammonium chloride and double iodide solution is employed, the alkali to be estimated being used in a sufficiently dilute solution to produce a yellow coloration only, the intensity of which is then compared in narrow, flat-bottomed tubes (smaller than those usually employed for performing Nessler's test) with a standard solution of sodium hydroxide, in like manner to the mode of estimating ammonia in dilute solution by means of Nessler's reagent. The method is inapplicable to solutions containing sulphides, as the darkening due to the formation of mercuric sulphide interferes with the yellow coloration. D. B.

Volumetric Estimation of Sodium Carbonate and Hydroxide in Commercial Caustic Soda. By H. GOEBEL (*Chem. Zeit.*, **13**, 696).—The following method has given good results:—The quantity of acid reqnired for neutralisation is ascertained by a preliminary experiment, and a quantity of standardised hydrochloric acid less than this is placed in a flask along with some phenolphthaleïn, the desired quantity of the solution of the soda under examination is dropped in, the whole diluted, and titrated cold until colourless. Poirrier blue is then added, and the titration in the cold continued

until the liquid is dark blne. The first titration gives the amount of hydroxide; the second, half the quantity of carbonate present.

D. A. L.

Estimation of Zinc in Manganiferous Flue Deposits. By E. JENSCH (*Chem. Zeit.*, **13**, 465, 726—727).—The customary method of estimating zinc in flue deposits is to dissolve in hydrochloric or sulphuric acid, oxidise with potassium chlorate or nitric acid, remove the excess of oxidising agent, and titrate the zinc by Schaffner's method with sodium sulphide in the ammoniacal solution, from which the iron and alumina have been removed. If previous to oxidation the acid solution is evaporated to a syrup, mixed with dilute acid, precipitated with ammonia, and oxidised by two or three hours contact with hydrogen peroxide, then not only is the excess of hydrogen peroxide much more readily got rid of than the chloride, &c., but also all the manganese, as well as the iron and alumina, is precipitated from solution. The author shows by numerous comparative experiments and analyses that in the other method the manganese was held in solution, and although it was gradually deposited, yet even after 168 hours, only 70 per cent. of it had separated, and in all the various analyses the missing manganese was found in the precipitate produced in the titration of the zinc, making the results too high.

D. A. L.

Use of Double Pyrophosphates in the Electrolytic Estimation and Separation of Metals. By A. BRAND (*Zeit. anal. Chem.*, **28**, 581—605).—Most of the metals, when their solutions are mixed with an excess of sodium or ammonium pyrophosphate, form soluble double pyrophosphates, and the solutions of these are not precipitated by ammonia or ammonium carbonate. The ammoniacal liquids so obtained are peculiarly suitable for electro-deposition. Nickel, cobalt, iron, and zinc are very satisfactorily deposited from solutions of the double pyrophosphates mixed with ammonium carbonate. Cadmium requires the presence of an abundant excess of ammonia. Metals which form peroxides behave differently. Manganese is deposited by a feeble current from a solution of manganese sodium pyrophosphate as peroxide, adhering firmly to the anode. It may be washed with distilled water (not with alcohol), ignited over the blowpipe, and weighed as manganoso-manganic oxide. Copper is best precipitated from a solution of the pyrophosphate in excess of sodium pyrophosphate, but this method presents no advantages over the use of an acid solution. For silver, the pyrophosphate solution acidified with nitric acid may be used, but it is in no way preferable to the cyanide solution. The mercuric double salt dissolved in ammonia or ammonium carbonate yields good results; mercurous salts must first be oxidised. Tin cannot be satisfactorily estimated by the electrolysis of the double pyrophosphates. Stannous solutions are easily reduced, but part of the salt oxidises at the anode, and the stannic salt produced requires a very strong current for its electrolysis; even then the results are low. Chromic salts are converted into chromic acid when electrolysed. If nickel or cobalt is present together with the chromium, it is completely precipitated; should, however, the solution contain chromic acid at the outset, neither

nickel nor cobalt can be thrown down. Iron also is reduced at first, but when chromic acid begins to appear the reduction ceases, and a reddish-yellow precipitate containing iron and pyrophosphoric acid appears at the cathode.

Lead and thallium cannot be precipitated from alkaline solutions without the formation of peroxide on the anode. In acid solutions this does not occur, but the rapid oxidation of the metal prevents an exact estimation. Bismuth is best thrown down from a solution containing ammonium oxalate. The acid bismuth solution is mixed with four or five times as much sodium pyrophosphate as is necessary for the formation of the double salt, then ammonium carbonate is added just to alkaline reaction, and then 3 to 5 grams of ammonium oxalate. Traces of peroxide are deposited on the anode. They are removed by adding a little oxalic acid towards the end of the operation. Antimony, although quantitatively deposited from a pyrophosphate solution mixed with ammonium carbonate, does not adhere firmly to the cathode.

Manganese may be separated from nickel, cadmium, zinc, and mercury by electrolysing a solution of the double salt mixed with 15 per cent. of concentrated ammonia. The manganese is deposited as peroxide on the anode, whilst the other metals adhere to the cathode. If iron or cobalt is present, a basic salt is deposited with the manganese. Manganese can be separated from metals which can be deposited from an acid solution, such as copper, cadmium, and mercury, by electrolysing such a solution containing pyrophosphoric acid, when the manganese remains dissolved as manganic pyrophosphate, and can subsequently be thrown down from the washings after concentration, reduction with oxalic acid, and addition of ammonia. The separation of manganese from iron and cobalt may be effected after the addition of ammonium oxalate to the pyrophosphate solution, as under these circumstances no manganese is thrown down as long as any ammonium oxalate remains undecomposed. Cadmium can be separated from zinc, iron, nickel, and cobalt by electrolysing a solution acidified with sulphuric acid. If manganese also is present, sodium pyrophosphate must be added before throwing down the cadmium. M. J. S.

Separation of Copper from Cadmium. By J. H. KASTLE (*Amer. Chem. J.*, **11**, 503—504).—It is proposed to precipitate the copper with metallic iron, the author preferring this to the method commonly used in qualitative analysis, which he thinks should be avoided by young students, as it involves the use of potassium cyanide. The filtrate from bismuth, if seen by its blue colour to contain copper, is acidified with nitric acid and evaporated to dryness. The residue is ignited until the nitrates are decomposed, and when cool treated with a few drops of hydrochloric acid; the solution is diluted and filtered into a test-tube, iron wire is added, and the whole heated at 80° in a water-bath. The copper is precipitated as a red deposit on the iron, and cadmium, if present, may be detected in the colourless solution by the yellow precipitate which it gives with hydrogen sulphide. C. F. B.

Analysis of Organic Substances containing Copper. By J. WALKER (*Ber.*, **22**, 3246—3247).—The analysis of copper salts of β-diketones and other substances containing the group $\cdot CO\cdot CH_2\cdot CO\cdot$, is attended with some difficulty, as they are slightly volatile, and if treated with nitric acid frequently explode. The author obtains good results by placing a weighed quantity of the salt in a Rose's crucible, and subjecting it to the action of a current of hydrogen sulphide in the cold. After 15—20 minutes, the crucible is heated to drive off the liberated ketone or its decomposition-products, the current of hydrogen sulphide is then stopped, and hydrogen passed over the heated cupric sulphide until it is converted into cuprous sulphide, in which form it is weighed. An estimation requires $1\frac{1}{2}$ hours. H. G. C.

Estimation of Iron by means of Potassium Permanganate in Hydrochloric Acid Solutions. By C. REINHARDT (*Chem. Zeit.*, **13**, 323—325).—After some tentative experiments, the following method was adopted :—$\frac{1}{2}$ to 1 gram of the finely pulverised and dry material is ignited until all the carbon or sulphur is expelled ; it is then dissolved in 25—30 c.c. of hydrochloric acid, sp. gr. 1·19, warmed, and reduced by gradually adding stannous chloride solution to slight excess. 60 c.c. of mercuric chloride solution is added to remove the excess of stannous chloride, and the whole mixed with about $1\frac{1}{2}$ litres of water containing 60 c.c. of a manganous sulphate solution containing free phosphoric and sulphuric acids and previously reddened with permanganate; then the iron is titrated with permanganate until a pink colour appears. The standard permanganate contains 6 grams per litre, the mercuric chloride 50 grams per litre, and the stannous chloride is made by dissolving 30 grams of tin free from iron in hydrochloric acid, filtering, and making up to 1 litre with moderately dilute hydrochloric acid, whilst for the manganous sulphate solution a mixture of 1000 c.c. of phosphoric acid, sp. gr. 1·3, mixed first with 600 c.c. of water, and then with 400 c.c. of sulphuric acid, sp. gr. 1·8, is poured into a solution containing 200 grams of crystalline manganous sulphate dissolved in a litre of water with the addition of a little dilute sulphuric acid, and the whole is made up to 3 litres. Special stopper arrangements for preserving the solutions are described. D. A. L.

Macro- and Micro-chemical Iron Reactions. By S. S. ZALESKI (*Zeit. physiol. Chem.*, **14**, 274—282; compare Abstr., 1886, 1054).—The importance of iron both in animal and plant life and the many important questions still unsettled in regard to it are pointed out. Before these can be investigated, however, it is important that we should have at hand reactions by which iron can be recognised in the tissues themselves. Observations on vegetable tissues are still wanting, but the reactions found most suitable for animal tissues and organs are those with potassium thiocyanate and hydrochloric acid, or with potassium ferrocyanide or ferricyanide and hydrochloric acid. The method adopted is the following :—A small piece of the tissue is allowed to remain for 24 hours in 65 per cent. alcohol, and then transferred for another 24 hours to 96 per cent.

alcohol, to which a few drops of yellow ammonium sulphide has been added. The piece of tissue becomes greenish, not only on the surface, but throughout its thickness, the intensity of the colour varying with the amount of iron present. It is finally transferred for a short time to absolute alcohol coloured with ammonium sulphide in order to complete the process of dehydration. Sections may then be cut with a microtome or by the hand. The sections are first soaked in 65 per cent. alcohol, and subsequently in a 1 per cent. solution of potassium ferrocyanide or ferricyanide for 24 hours, or for two or three days in potassium thiocyanate dissolved in 96 per cent. alcohol. The sections are then placed in 1 to 2 per cent. hydrochloric acid in 96 per cent. alcohol for 24 hours, then in absolute alcohol, and finally mounted permanently; or the whole piece of tissue may be soaked in these reagents successively before the sections are made. Whole embryos, or even small animals, may be similarly stained in bulk.

W. D. H.

Estimation of Iron in Blood. By L. Lapicque (*Bull. Soc. Chim.*, [3], 2, 295—297).—Blood (2 grams) is warmed in a flask with pure sulphuric acid (3 c.c.), a few drops of nitric acid are added, and after slight heating the liquid is dilnted with water and boiled for a few minutes; to the cooled liquor after dilution to 40 c.c. with distilled water, 10 c.c. of a 20 per cent. solution of ammonium thiocyanate is added, and the amount of iron present is ascertained by means of Duboscq's colorimeter.

T. G. N.

Estimation of Nickel by Precipitation as Sulphide. By A. Lecrenier (*Chem. Zeit.*, 13, 431; 449—450).—The precipitation of nickel as sulphide by ammonium snlphide is not complete when the latter contains any polysulphides. The author now finds that by using 2 vols. of a 10 per cent. solution of sodium sulphite to 1 vol. of ammonium sulphide solution and heating on a water-bath, the polysulphides disappear in a few minutes; but even this solution only produces complete precipitation of nickel as sulphide when the solutions do not contain less than 0·1 gram of nickel to 200 c.c. of water. The complete precipitation of the nickel by this colourless ammonium sulphide may be ensured even from very dilute solutions by adding ammonium carbonate, chloride, or acetate, &c. Ammonia prevents the precipitation of nickel sulphide, either partially or entirely according to the strength of the solutions, therefore with certain concentrations, colourless solutions may be obtained containing both a nickel salt and ammonium sulphide. With ammoniacal solutions, it is therefore advisable to boil off the greater part of the ammonia and to neutralise the rest with carbonic anhydride, or the ammonia may be neutralised by an acid and the solution made alkaline by adding ammonium carbonate. For analysis, the nickel sulphide is dissolved in aqua regia and determined electrolytically.

The author considers the retention of nickel sulphides in solution is due to the formation of an ammonium thionickelate, in support of which view he adduces the following facts:—

1. In the absence of oxidising influences, ammonium sulphide

decolorised by mercury completely precipitates nickel sulphide from solutions of any dilution. 2. Pure ammonium hydrosulphide (free from ammonia) saturated with sulphur dissolves nickel sulphide completely, probably indicating the formation of a higher sulphide of nickel, and although sodium sulphite prevents the solution of nickel sulphide, yet a solution of the latter in ammonium polysulphide is not precipitated by boiling with the former. Therefore when once the higher sulphide has formed and combined with the ammonium sulphide, the sodium sulphite cannot decompose it; ammonium thiostannate behaves in a similar manner. D. A. L.

Volumetric Estimation of Chromium in Chrome-iron Ore. —By C. Reinhardt (*Chem. Zeit.*, **13**, 430).—For estimating chromium in chrome-iron ore volumetrically, the author, after fusing with a mixture of soda-lime and potassium chlorate, dissolves in water, adds hydrochloric acid, or sulphuric acid if much manganese is present, warms and reduces with a measured quantity of ferrous sulphate (25 grams per litre) solution, and titrates back, using the permanganate and manganous sulphate previously recommended (this vol., p. 296), the end reaction being violet in this case. D. A. L.

Analytical Examination of Water for Technical Purposes. By A. H. Allen (*J. Soc. Chem. Ind.*, **7**, 795—806).—The author contends that although Clark's process for determining the hardness of water gives constant and fairly accurate results when applied to certain waters of moderate hardness, it gives misleading results when applied to hard water, highly magnesian water, or waters outside the general run of those met with in the south of England. In such cases the soap test must be abandoned in favour of other methods which furnish the information required more accurately, such for instance as boiling down the water to a small bulk with sodium carbonate, filtering and washing the precipitate, dissolving it in standard acid, and titrating back with standard alkali and methyl-orange. The result represents the total calcium and magnesium very closely, and may be expressed in terms of calcium carbonate. By titrating the original water with standard acid and methyl-orange, an estimate of the earthy carbonates (temporary hardness) can be obtained in a few minutes. The author gives many valuable analyses of special waters, the results of which furnish the strongest proofs of the untrustworthy nature of the soap test. In the remaining part of the paper the author discusses at some length the question of stating the results of the analysis of waters, which in his opinion should depend on circumstances. For technical purposes, grains per gallon seems to be the most generally convenient mode of expression, although in the case of feed waters it is often useful to add another table showing pounds per 1000 gallons. With regard to the method of recording acids and bases in combination as salts, a more regular and generally accepted practice is desirable. In the case of sulphates the author is in favour of expressing all the calcium as $CaSO_4$, or at any rate all which is in excess of that required to form carbonate

assuming of course that the sulphates are present in excess. The combined carbonic anhydride should as far as possible be expressed in the form of calcium carbonate. D. B.

Estimation of Alkalis in Water. By F. MUCK (*Zeit. anal. Chem.*, **28**, 628).—A rough method in use consists in converting all the bases into sulphates and deducting from the gross weight that of the silica and the calcium and magnesium sulphates. The water is evaporated to dryness, and the residue is moistened with alcohol containing about three drops of concentrated sulphuric acid per c.c. The alcohol is then set on fire and burnt off, when, if the quantity of acid added is sufficient, the residue will appear damp, and acid fumes will be given off. In the contrary case, the residue will remain dry and will require a repetition of the treatment with the acid alcohol. In this way the quantity of acid is very conveniently adjusted. The final ignition with ammonium carbonate is performed as usual. M. J. S.

Estimation of Methoxyl. By R. BENEDIKT and A. GRÜSSNER (*Chem. Zeit.*, **13**, 872—873).—The authors describe and illustrate an apparatus which answers well for the estimation of methoxyl by Zeisel's method. A distilling flask serves for the reaction, carbonic anhydride being conducted to the bottom by a tube passing through a cork in the neck, the side tube bends upwards and terminates in a neck, into which is fitted, by a cork, the end of an upright tube which continues to a series of three bulbs, one above another; the first (lowest), of 30 c.c. capacity, is connected with the second, 80 to 100 c.c. capacity, by a tube projecting well into the latter, whilst a tube starts from the bottom of the second and terminates in a downward bend about midway in the third bulb, which has the same capacity as the second; above these three bulbs there is another, but much smaller bulb, and then a long tube, bent twice at right angles, passing downwards into the absorption apparatus consisting of a distilling flask connected by its side tube, which is bent downwards for the purpose, with a second flask. When in operation, the three bulbs are surrounded by a condenser, the second and third being charged by means of a wash-bottle with amorphous phosphorus and water; water at 70° is caused to circulate in the condenser, and by means of the bulbs the water and almost all the hydriodic acid run back into the reaction flask, the iodine is washed out, and the methyl iodide and carbonic anhydride pass on to the absorption apparatus. By retaining the condenser at 89°, isopropyl iodide has been successfully carried to the absorption flasks. D. A. L.

Estimation of Glycerol. By T. MORAWSKI (*Chem. Zeit.*, **13**, 431).—About 2 grams of glycerol is weighed into a crucible containing from 50—60 grams of lead oxide, and sufficient alcohol is added to permit of the mass being well mixed; it is dried in a vacuum water-oven and then heated at 120—130° to constant weight. The results differ by 0·5—0·6 per cent. on an average, and judging from a

table of numbers obtained by various means, this method gives results agreeing fairly well with numbers obtained by combustion, &c.

D. A. L.

Estimation of Glycerol in Crude Glycerol. By J. Lewkowitsch (*Chem. Zeit.*, **13**, 659).—The author has already found the Benedikt-Cantor acetin method (Abstr., 1889, 748) effective, and now gives results, confirming that view, obtained with crude glycerols of various origins; moreover, from these results he recommends the adoption of the method in all cases where a more or less pure crude glycerol is obtained in course of analysis, as, for instance, in the glycerol estimations in fats or in wine or beer analyses. The author has estimated the glycerol in the fat of Sawarri nut, obtaining 88·48 and 88·29 per cent. of pure glycerol; the method does away with the waiting for drying, and also the ash determinations. The author neither considers nor has he found the lead oxide method (Morawski, preceding abstract) trustworthy for crude glycerols, at least in its present form. D. A. L.

Examination of Commercial Carbolic Acid and of Disinfectant Powders made therefrom. By R. Williams (*J. Soc. Chem. Ind.*, **7**, 826—828).—Most of the commercial carbolic acid examined by the author was found to contain little or no phenol, but consisted of cresols and still higher homologues. For the estimation of the water in carbolic acid, the distillation method is the most accurate. In the case of carbolic acid powders, the percentage of tar acids may be determined by the following process devised by the author, which is said to be simple in execution, yield accurate results, and to be applicable to a large number of samples at the same time:—600 grains of the sample is placed in a stoppered bottle, and digested for one or two hours with 3000 grains of strong alcohol, the mixture being shaken frequently. It is then passed through a double filter, after which two-thirds of the whole is transferred to a 10-oz. porcelain basin. 300 grains of a 10 per cent. solution of sodium hydroxide is now added, and the mixture evaporated until all the alcohol has been expelled. The residue is transferred to a long, narrow tube, holding 1000 grains, and carefully graduated into 500 divisions. 100 grains of hydrochloric acid is added, and the liquid saturated with salt. After mixing well and allowing to coo[l] to 15°, the volume of tar acids is read off. As the sp. gr. of these acids usually lies between 1·04 and 1·05, their approximate weight may be ascertained by adding one-twentieth to the volume found.

D. B.

Percentage Glucosometer. By A. W. Gerrard (*Lancet*, 1890, 1, 15—16).—This instrument is designed to enable medical practitioners to determine rapidly by means of Fehling's solution the percentage of dextrose in diabetic urines. It consists of a pair of burettes, clasped by a pair of swinging arms supported on an upright brass stand; the burettes can be moved at will, so as to be brought over a dish containing 10 c.c. of boiling Fehling's solution diluted with water. The burettes are graduated in degrees which correspond with per-

centages of dextrose in a urine diluted to 20 volumes with water. The instrument indicates percentages between 1 and 10; and the two burettes are of different sizes, one thin and narrow for high percentages, the other of larger capacity for low percentages. The saving of time to the busy practitioner thus accomplished is obvious.

W. D. H.

Analysis of Sugars. By E. JUNGFLEISCH and L. GRIMBERT (*Compt. rend.*, **109**, 867—870).—The authors have previously shown (Abstr., 1889, 479) that feeble acids do not affect the rotatory power of levulose, but that strong acids produce considerable variations, the effect being greater when the levulose is formed by inversion in presence of the strong acid than when the latter is added to levulose previously prepared. This action of the strong acids introduces serious errors into Clerget's inversion method for the analyses of sugars, and the use of acetic acid for producing inversion has been adopted by some chemists.

The authors find that although alkaline acetates have no influence on inversion by strong acids, they prevent complete inversion by acetic acid, even when the latter is used in large excess. Alkaline citrates, formates, lactates, and tartrates, and zinc and lead acetates, produce a similar effect, but calcium acetate is much less injurious. Salts of the strong monobasic acids do not affect inversion by acetic acid. Normal salts of bibasic acids interfere when they contain monad metals, but not when the metals are dyad. Acid salts of strong polybasic acids do not interfere, and some of them, like the acid sulphates and acid oxalates, can themselves produce inversion. C. H. B.

Estimation of Raffinose in Raw Sugar. By T. BREYER (*Chem. Zeit.*, **13**, 559—560).—50 c.c. of the solution for polarisation, containing 26·048 grams per 100 c.c., is mixed with 5 c.c. of hydrochloric acid, sp. gr. 1·182, in a 50—55 c.c. flask, which is then placed in a water-bath, along with a similar flask filled with water, and with a thermometer in it; the heat is regulated so that this thermometer registers 68—69° for five minutes, five minutes being allowed for it to reach this temperature. The solution is then quickly cooled, and removed to the polarising room; after some hours, the flask is filled to the mark, decolorised with dry animal charcoal if necessary, and polarised in a cylinder with a tube for the thermometer attached. The apparent amount of saccharose can be calculated by Clerget's formula from the polarisation before and after inversion and the thermometer readings. In the absence of substances reducing Fehling's solution, and with a difference of 0·5 or above from the direct polarisation indicating the presence of some other optically active substance, the actual amount of saccharose can be calculated by a formula given in the paper, which is a combination of Clerget's and Creydt's formulæ. The difference between the number so found and the direct polarisation may be assumed to be due to a definite quantity of raffinose, which may be calculated. It is shown that neither differences in concentration nor in temperature, within certain

limits, will affect Creydt's constants for the inversion of raffinose solutions, but if greater refinement is required, a formula embodying the necessary corrections is given. D. A. L.

Detection of Rye-Meal and Bran in Wheat-Meal and Bran. By F. BENECKE (*Landw. Versuchs.-Stat.*, **36**, 337—366).—The method proposed by the author is based on the fact that whilst the ripe rye-corn of nearly every description contains a blue colouring matter, that of wheat does not (with the exception of one unimportant variety). To determine whether wheat-bran is free from rye-bran, or whether rye-bran is very much adulterated with wheat-bran, the product is so finely ground as to pass through a millimetre sieve; the meal is then sifted off through fine muslin, and the remaining bran (about a teaspoonful) rubbed with ether, until the ether is made only slightly turbid. It is then washed into a beaker with ether, the ether poured off, and olive oil added. It is then examined by a microscope magnifying from 100 to 200 times. To find how much rye-bran is mixed with wheat-bran, the relation of coloured to colourless particles in 100 units of surface is determined. It is possible to detect the presence of rye-bran without a microscope by putting the olive-oil containing the bran on a glass plate over a white surface.

The following method was found to be the easiest and most trustworthy for the determination of rye-meal in wheat-meal:—100 grams of the meal is put into a pear-shaped vessel (500—600 c.c. capacity), which is then two-thirds filled with chloroform. The whole is well shaken, so as to distribute the meal equally, and the vessel nearly filled with chloroform, again shaken, and allowed to settle. The dirt and dust settle first, and after about 24 hours a further separation takes place. With rye- and wheat-meal, the gluten settles to the bottom, whilst the other constituents, especially the starch, form a solid, floating mass. Between the sediment and the floating portion is a more or less clear, yellow chloroform solution. The differences in colour of the sediments and floating portions from the two kinds of meal is very striking, and is shown, as well as that of various mixtures, in coloured tables. For instance, the colour of the residue from rye-meal of poorest quality is dark olive-green, and the floating portion light-brown; with wheat of best quality, the colours are brownish-yellow and almost white respectively. A further difference is that the amount of sediment with rye-meal of worst quality is far greater than that of the best wheat-meal. The better kinds of meal give less sediment. Whilst the amount of sediment depends on the quality of the meal, the colour depends on its origin.

To detect with certainty the presence of 10 per cent. of rye-meal of best quality in wheat-meal of second quality, the floating portion is carefully stirred and washed out with chloroform; ether is then poured into the vessel, the sediment stirred up, washed into a dish, and allowed to settle; the ether is poured off, moderately strong acetic acid is added, and the whole boiled and stirred; wheat-meal so treated gives a yellowish-brown colour, rye a splendid, deep rose-red colour (shown in the table). The colours produced with various mixtures are also shown.

Adulteration of wheat-meal with rye-meal is less frequent than than that of rye with wheat; but the above method, owing to its trustworthiness and ease with which it is used, is of considerable value. N. H. M.

Estimation of Cellulose. By G. LANGE (*Zeit. physiol. Chem.*, **14**, 283—288).—The method depends on the fact that cellulose remains unaltered after fusion with alkaline hydroxides.

10 grams of the material is mixed with 30—40 grams of an alkaline hydroxide and 30—40 c.c. of water in a retort which is heated at 140—180° for an hour; it is then cooled to 80°, and the contents of the retort washed out with hot water and finally with cold water into a beaker. The mixture is here acidified with dilute sulphuric acid, and again carefully made just alkaline with dilute sodium hydroxide, so that all substances precipitated by the acid enter into solution again with the exception of the cellulose; the precipitate is collected on a filter, weighed, incinerated, and the amount of ash deducted. The method gives very concordaut results; they are a little higher than those obtained by F. Schulze's method (*Chem. Centr.*, 1857, 321). W. D. H.

Valuation of Wine-lees. By P. BOESSNECK (*Chem. Zeit.*, **13**, 356—357).—Goldenberg's, Fresenius's, and v. Lorenz's methods are individually inaccurate for the estimation of total tartaric acid in wine-lees, but concordant results are obtained by a combination of the Goldenberg-Geromont and Fresenius methods. 10 grams of the finely-powdered wine-lees is digested for some hours, with frequent agitation, in 15 c.c. of hydrochloric acid, sp. gr. 1·1, and the same volume of water, and made up to 203 c.c.; it is then filtered, and 100 c.c. heated, made strongly alkaline with potash, and, after prolonged boiling, again filtered. The filtrate and washings are treated with hydrochloric acid until only feebly alkaline, evaporated to 20 c.c., and when cold treated with 5 or 6 c.c. of glacial acetic acid. After 10 minutes' warming, 100 c.c. of absolute alcohol is poured in, and in two hours' time it is filtered. The precipitate, consisting of all the tartaric acid of the lees as potassium salt, is washed free from acid with strong alcohol, and titrated at first to neutrality, and then, after boiling for some time, to the finishing point, using the artificially-prepared litmus-colouring matter, "azolitminum." Potassium hydrogen tartrate may be determined in the presence of gypsum by boiling with excess of antimonious anhydride and estimating the antimony in the filtrate containing the potassium tartrate as the potassium antimony salt; or the whole of the tartaric acid may be determined by treating the lees first with potassium oxalate to eliminate calcium, then boiling with antimonious anhydride and decomposing the potassium antimony oxalate with gypsum, finally estimating the antimony in the filtrate. The strength of the solution and the quantity of antimonious anhydride present influence the results. The use of litmus tincture in the v. Lorenz method is not approved of. D. A. L.

Analysis of Argol. By N. v. LORENZ (*Chem. Zeit.*, **13**, 693—694; compare Abstr., 1888, 327, and preceding abstract).—The author

criticises in detail Goldenberg's methods of estimating tartaric acid, and asserts their untrustworthiness, but upholds the efficiency of his own method; he experiences no difficulty in using litmus tincture as an indicator, and attributes the failure of other chemists to the use of litmus either of inferior quality or not prepared according to his directions. He regards the Grosjean-Warington and the Sheurer-Kestner processes as even less trustworthy for the purpose than the Goldenberg method. D. A. L.

The Fokker-Salkowski Method of estimating Uric Acid in Normal and Pathological Urines. By R. POTT (*Pflüger's Archiv*, **45**, 389—400).—Fokker's method of estimating uric acid was compared with Salkowski's; in some cases the two methods gave identical results, in others they did not; the highest percentage difference obtained was about 3. It was generally much less. The results were sometimes higher by one method, sometimes by the other. Such variations are not, however, regarded as very serious, and the cause of their occurrence is not apparent. The experiments were performed with normal and with various kinds of morbid urine, and the final conclusion is that Fokker's method of estimating uric acid is applicable to all kinds of urine. W. D. H.

Simplified Fat-extraction Apparatus. By J. T. CRAWLEY (*Amer. Chem. J.*, **11**, 507—508).—This consists of (1) a glass tube 4 cm. wide and 20 cm. long, drawn out at one end so as to pass through a rather large hole in the cork of a flask; (2) a large sized test-tube, fitting into the larger tube so as to reach within 3 cm. of the top; (3) a glass tube of about $\frac{1}{3}$-cm. bore, bent so that one end dips down to the bottom of the test-tube, whilst the other limb lies between the two tubes (1) and (2) with the other end reaching to the narrowed part of the outer tube. The upper part of (1) is connected with a condenser, and ether or alcohol is boiled in the flask, the substance under examination being placed in the test-tube. The vapour is condensed, and flows back into the test-tube, and when this is nearly full, capillary attraction draws the liquid through the syphon, and the contents of the test-tube with the extracted fats are syphoned off into the flask below. C. F. B.

Estimation of Fat in Sour Milk. By M. KÜHN (*Chem. Centr.*, 1889, ii, 303; from *Milch-Zeit.*, **18**, 561—562).—The sour milk is rendered just alkaline with aqueous potash (40 grams in 1 litre of water), thereby dissolving the caseïn. 10 grams of the alkaline milk is poured on to a mixture of 25 grams of ignited gypsum, 4 grams of precipitated calcium carbonate, and 2 grams of potassium hydrogen sulphate, dried, ground up, and extracted in a Soxhlet's extractor. The addition of potassium hydrogen sulphate prevents the slight excess of alkali from saponifying the butter fat, whilst the calcium carbonate neutralises the remainder of the potassium hydrogen sulphate. J. W. L.

Rapid Estimation of Fat in Milk. By A. W. STOKES (*Chem. News*, **60**, 214—215).—The author finds the following method, sug-

gested by W. Schmid, to be rapid and accurate. 10 c.c. of milk is pipetted into tubes partly graduated up to 50 c.c., hydrochloric acid is poured in roughly to the 20 c.c. mark, the mixture is boiled, not more than two minutes, with frequent shaking, until it turns brown (watered milks do not turn deep-brown, whilst condensed or sugared milks become almost black); then after about three minutes it is cooled, and the tube filled up roughly with ether to 50 c.c., corked, and shaken for half a minute. In five minutes' time, 20 c.c. of the ethereal solution is carefully pipetted off, evaporated, and the fat dried in an air-bath and weighed. The volume of ether left in the tube is read off, taking three-quarters of the stratum of caseïn, if any is present, as ether, and the fat calculated on the whole volume of ether, &c. The differences between the fat observed by this method and the fat calculated never reaches a tenth per cent. D. A. L.

Examination of Butter. By S. SALVATORI (*Bied. Centr.*, **18**, 788; from *Staz. Sper. Agrar. Ital.*, **14**, 516—526).—Dronot's method for examining butter consists in melting it slowly, when, if the butter is pure, a clear liquid is obtained, the water and caseïn settling at the bottom; an artificial butter, on the other hand, remains turbid, and only becomes clear when heated much above its melting point. The author finds that the method is not always trustworthy, inasmuch as purified natural fats of all kinds, oleomargarin, and frequently natural butter give very clear liquids, natural butter being further characterised by a sediment; the latter, in artificial butters, is amorphous, and renders the liquid turbid as it settles slowly. Some melted samples of natural butter were also turbid, from the presence of drops of water. When natural is mixed with artificial butter, the addition of margarin or fat cannot be established with certainty.

N. H. M.

Rapid Method for the Analysis of Tallow. By H. TAFFE (*Bull. Soc. Chim.* [3], **2**, 209—210).—Ordinary tallow, when titrated for free stearic acid, yields 3·6 per cent., whereas stearine candles of good quality yield 100 per cent.; olive oil yields 2·5 per cent. of free oleic acid.

The method consists in determining the acid factor for a solution of the fat in an already titrated olive oil by means of normal potash, using turmeric as an indicator. T. G. N.

Analysis of Wool Oils. By H. HORWITZ (*Dingl. polyt. J.*, **271**, 29—30).—The materials used in the manufacture of woollen goods for imbuing the fibres intimately with oil are emulsions of liquid fats and aqueous alkaline solutions. Those examined by the author were mostly mixtures of olive and cotton-seed oils with solutions of ammonia and sodium hydroxide. As olive oil is often adulterated with mineral, resin and drying oils, which have an injurious effect on the subsequent manufacturing operations, the author recommends the following process for the quantitative estimation of these adulterants:—1·5 to 2 grams of the oil is weighed in a closed vessel, and digested for some hours with alcohol and ether. The sodium hydroxide, which remains undissolved, is collected on a tared filter,

dried at 100°, and weighed. One half of the filtrate is evaporated and dried at 100—120°, in order to obtain the fat, whilst in the other half the ammonia is determined by treating the solution with hydrochloric acid and precipitating with platinic chloride. The water is determined by drying another portion of the oil at 100—120°, weighing, and deducting from the weight the quantity of ammonia found. The following analysis is given as an example:—

Fat.	Sodium hydroxide.	Ammonia.	Water.
14·16	0·91	0·32	84·45

showing that for the preparation of the wool oil in question 14·16 parts of fat, 0·91 part of soda, and 84·77 parts of ammonia of sp. gr. 0·9983 had been used. D. B.

Examination of Commercial Oleïn for Linoleïc Acid. By K. HAZURA (*Zeit. ang. Chem.*, 1889, 283—284; compare Abstr., 1887, 359, 798, 913; 1888, 816, 817, 1269, 1270; 1889, 374).—Olive oil contains chiefly oleïc acid, with a small quantity of linolic acid, $C_{18}H_{32}O_2$. On oxidising its alkaline solution with potassium permanganate, the products are *dihydroxystearic acid* (melting point 137°; almost insoluble in water and ether), *sativic acid*, $C_{18}H_{32}O_2(OH)_4$ (m.p. 173—175°; slightly soluble in water, insoluble in ether), and *azelaïc acid*, $C_9H_{16}O_4$ (easily soluble in water and ether). The acid of linseed oil consists mainly of *linolenic acid* and *isolinolenic acid*, $C_{18}H_{30}O_2(OH)_6$, with small quantities of oleïc and linolic acids. The solid products of oxidation are dihydroxystearic acid, sativic acid, azelaïc acid, and two hexahydroxystearic acids, $C_{18}H_{30}O_2(OH)_6$, namely, *linusic acid* (m.p. 203°; completely insoluble in ether, sparingly soluble in water), and *isolinusic acid* (m.p. 173°; soluble in water, but insoluble in ether).

50 grams of the oil is saponified with alcoholic potash, freed from the alcohol, and diluted to 1 litre. To the solution, which must be strongly alkaline, there is then added a litre of 5 per cent. solution of potassium permanganate. After an hour it is filtered; the filtrate is acidified with sulphuric acid, filtered, neutralised with potash, evaporated to 300 c.c., and again acidified, whereupon a second precipitate is obtained. The whole is then shaken with ether, when, if the precipitate dissolves, it consists of azelaïc acid, and the oil was free from linoleïc acid. If it does not dissolve, it is collected, crystallised once or twice from water or alcohol, and its melting point determined. If this is above 160°, linoleïc acid was certainly present. Less than 1 per cent. cannot, however, be detected. M. J. S.

Estimation of Fat in Poppy-cake. By P. BAESSLER (*Landw. Versuchs-Stat.*, 36, 367—372).—It was previously shown (Abstr. 1889, 321) that too low results are obtained when the fat of linseed cake is determined after drying the substance at 100°, and experiments described in the present paper show that the same holds good with poppy-cake. For example, a sample of cake containing 7·54 per cent. of fat (when dried for 4 to 6 hours at 110° in a stream o

hydrogen) lost 0·84 per cent. when heated for two hours, 3·11 per cent. when heated for four hours, and 3·67 per cent. when heated for six hours at 100° in air; at 110° the loss was still greater. Determinations made after drying in a vacuum over sulphuric acid were also unsatisfactory, the results being in one case 1·10, and in another 0·31 too low.

With regard to the determinations of water, it is found that when the substance is heated at 100° in a stream of dry hydrogen and the water weighed, the results obtained are too high, owing to an oily substance being carried over into the absorption apparatus.

The best results, both with regard to water and fat, were obtained by heating the substance from two and a half to three hours at 90°.

N. H. M.

Estimation of Cotton-seed Oil in Lard. By BOCKAIRY (*Bull. Soc. Chim.* [3], **2**, 310—313; compare this vol., p. 93).—The sp. grs. of the following substances at 50° are :—

Lard	0·889—0·8915	Ox-kidney fat......	0·8895
Rancid lard........	0·8895	Fresh cotton-seed oil	0·897
Oleostearine........	0·8885	Old ,, ,,	0·896

and mixtures of cotton-seed oil with pure lard determine a proportionate rise in the density.

Hübl's iodine test does not give sufficiently accurate data with the crude mixtures, but the author finds that the iodine numbers given by the solid fatty acids separated from these mixtures are more satisfactory, and he is working on a process for this estimation.

T. G. N.

Iodine Absorption as a Test for Essential Oils. By H. W. SNOW (*Pharm. J. Trans.* [3], **20**, 4; compare this vol., pp. 199, 200).—Determinations are given of the iodine absorptions of a number of essential oils. The process followed was Hübl's, but the author found that the absorption was usually not complete in less than 40 hours. The experiments have shown that although these iodine absorptions are not constant, they afford valuable indications in determining the purity of oils, and they may be directly employed for the detection of turpentine in oil of peppermint. R. R.

Detection of Ordinary Turpentine in Venice Turpentine. By E. HIRSCHSOHN (*Arch. Pharm.* [3], **27**, 999—1000, from *Pharm. Zeit. Russ.*, **36**, 561).—The behaviour of turpentine towards ammonia not only affords a certain means of discriminating between the two kinds of turpentine, but up to a certain point serves to detect one variety in presence of the other.

A small quantity of ordinary turpentine treated with strong ammonia gradually mixes to form a milk; with Venice turpentine the liquid remains clear. If a glass rod is used to stir up the mixture, the Venice turpentine gradually becomes a semi-solid, colourless, opaque mass, whilst the liquid is only slightly turbid; ordinary turpentine, on the other hand, dissolves readily and forms a milky liquid, which after a short time sets to a jelly, especially when 5 parts of ammonia is added to 1 part of turpentine. Venice turpentine containing 50 per

cent. of ordinary turpentine is readily disseminated through ammonia; the mixture sets after five minutes, and when placed in boiling water becomes clear; a mixture of 30 per cent. of ordinary turpentine behaves similarly, sets in about 10 minutes, and becomes clear on the water-bath; with 20 per cent., the mixture readily becomes milky, does not set, but becomes clear on the water-bath; mixtures containing less than 20 per cent., can only be detected by comparison with genuine Venice turpentine. Mixtures containing not less than 30 per cent. of ordinary turpentine can to some extent be detected by the use of 80 per cent. alcohol; on shaking up 1 part of turpentine with 3 parts of alcohol, Venice turpentine gives an almost clear solution, whilst with ordinary turpentine over half the quantity employed separates after a short time. J. T.

Estimation of Urea. By E. PFLÜGER and L. BLEIBTREU (*Pflüger's Archiv.*, **44**, 1—116).—This is a series of six articles related one to the other. The first two are by E. Pflüger alone, and relate to technical details, whilst the next four deal with the actual analyses, full details of which are given; the outcome of the whole is the comparison of three methods of urea analysis, Bunsen's method (compare Böhland, Abstr., 1889, 538), the method of heating with caustic alkali, and lastly the phosphoric acid method. Bunsen's method with Böhland's modifications, and with certain precautions fully detailed in the present communications, is one of the greatest possible accuracy. The alkali method is simpler, but yields somewhat less ammonia even if the heating is continued for six hours. The phosphoric acid method is far simpler than either, and although it gives somewhat higher results than Bunsen's method, is regarded as being sufficiently accurate for most purposes. The apparatus and reagents necessary are:—a Schlösing-Neubauer apparatus for the estimation of the preformed ammonia in urine; copper drying chamber of special construction, which is fully described; a distilling apparatus; solution of sulphuric acid, of such a strength that 1 c.c. corresponds with 0·001 gram of nitrogen, an equivalent solution of sodium thiosulphate; a 20 per cent. solution of potassium iodide, and a 4 per cent. solution of potassium iodate; a mixture of hydrochloric and phosphotungstic acids; phosphoric acid in crystals, or a strong solution of phosphoric acid. The method is briefly as follows:—1 volume of urine is mixed with 2 volumes of the acid mixture to remove "extractions;" this is allowed to remain for 24 hours, and filtered into a mortar (filtrate I). This is rubbed up with chalk until alkaline, covered with a glass plate until the blue colour disappears, and filtered (filtrate II); three burettes are filled with this filtrate and closed with good stoppers. Some of this filtrate serves for the estimation of preformed ammonia. 10 grams of phosphoric acid crystals is placed in each of four distilling flasks, and 15 c.c. of filtrate II added. The flasks are then placed in the oven and heated for three hours to a temperature of 230—360°. To each about 70 c.c. of sodium hydroxide of 1·3 sp. gr., and 600 c.c. of water are added, and the distillate received in a measured volume of the standard sulphuric acid, which is then treated with iodine and thiosulphate, and from the amount of this used the nitrogen from urea

and ammonia is calculated; the ammonia is known, and can be subtracted from this. The average is thus taken of the four estimations. W. D. H.

In the same volume (pp. 273—300) is an article by Pflüger relating to the details and precautions necessary in the titration of acids and bases, especially of ammonia, by means of iodine and thiosulphate. W. D. H.

Analysis of Methylanilines. By H GIRAUD (*Bull. Soc. Chim.* [3], **2**, 142—144; compare Abstr., 1889, 1038).—The author objects to the process described by Reverdin and De la Harpe (Abstr., 1889, 1038), on account of the difficulty in procuring and of preserving absolute acetic anhydride, and recommends the employment of a 10 per cent. solution of this substance in dimethylamine, which is easily standardised by barium hydroxide, using phenolphthaleïn as an indicator. The analysis of a sample is thus conducted:—1 gram of the methylaniline is added to 10 c.c. of the above acetic anhydride solution, and allowed to remain one hour in contact, when the mixture is to be diluted with water and titrated; the difference in the two values for acetic anhydride determining the methylaniline present.

The author also states that the formation of nitro- and of nitroso-nitrosamines in Nölting's process, noticed by the above-mentioned authors, is probably due to their employing too great an excess of nitrite. T. G. N.

Test for Antipyrin. By A. C. STARK (*Pharm. J. Trans.* [3], **19**, 949).—The green colour produced when a liquid containing antipyrin is added to sulphuric acid with which a little weak solution of potassium nitrate has been mixed, is a delicate and characteristic test. R. R.

Estimation of Cinchona Alkaloïds. By T. FAWSSETT (*Pharm. J. Trans.* [3], **19**, 914).—1 gram of the alkaloïd or salt is dissolved in just sufficient dilute sulphuric acid, and the solution is diluted to 600 c.c., in a cylindrical vessel at a temperature not much below 15°. Bromine-water, which has immediately before been standardised in the usual way, is run in in quantities of 5 c.c., the colour being allowed to disappear after each addition, until a permanent yellow tint is produced. The excess of bromine is estimated colorimetrically by determining the quantity of the bromine-water required to produce an identical tint in 600 c.c. of pure water contained in a similar vessel. The amount of bromine decolorised by the alkaloïd is easily calculated. It was found that the amount of bromine absorbed by each molecule of quinine, quinidine, and cupreïne was 6 atoms; 4 atoms by a molecule of hydroquinine, 2 atoms by each molecule of cinchonidine cinchonine, and amorphous quinine. The average amount of bromine absorbed by 1 gram of various specimens of commercial sulphate of quinine was found to be 1·029 gram. The process gives constant and accurate results, the maximum error found by control experiments being only 0·008 gram of bromine. R. R.

Estimation of Alkaloïds in Coca Leaves. By V. D. MARK (*J. Pharm.* [5], **20**, 500; from *Pharm. Zeits. Russ.*, **28**, 1889, 349).—50 grams of the powdered leaves and 20 grams of calcined magnesia are moistened with a little water, dried at 60°, and exhausted with ether. The ether is removed by distillation, and the residue treated with 2 per cent. hydrochloric acid; after filtering, the filtrate is shaken with a little ether, just sufficient to remove the colouring matter; ammonia in excess is now added, and again ether. This last operation is repeated three times, employing 25 c.c. of ether each time. The ethereal liquids are mixed, and freed from the small quantity of water they may contain by the addition of some fragments of fused calcium chloride. Finally, the ether is removed by evaporation, and the residue dried and weighed. J. T.

Cinnamylcocaïne in Coca Leaves. By B. H. PAUL and A. J. COWNLEY (*Pharm. J. Trans.* [3], **20**, 166).—The amount of cocaïne in coca leaves cannot be determined by the amount of alkaloïd crystallisable from light petroleum, for the authors have found that the leaves contain also cinnamylcocaïne, which is similarly crystallisable. R. R.

Assay of Emetine in Ipecacuanha Wine. By T. P. BLUNT (*Pharm. J. Trans.* [3], **20**, 254).—This method depends on the fact that emetine removes mercuric iodide from its solution in potassium iodide, and that it is therefore possible to measure the amount removed by determining the solvent power of the liberated potassium iodide for mercuric iodide. Practically the method employed is to add a standard solution of mercuric chloride until a permanent precipitate is obtained.

50 c.c. of the wine is evaporated on the water-bath to 20 c.c., then 10 c.c. of Mayer's solution is added; the precipitate is allowed to settle, and the liquid passed through a dry filter. To the 25 or 27 c.c. of filtrate thus obtained, a centinormal solution of mercuric chloride is gradually added from a pipette until a faint permanent cloudiness is obtained. From 4 to 6 c.c. will be required, according to the amount of emetine present.

Mayer's solution is prepared by adding saturated mercuric chloride solution to 100 parts of a 10 per cent. solution of potassium iodide until there is a slight permanent precipitate, filtering, and making up to 200 parts with water. R. R.

Reactions of the Alkaloïds. By A. L. BROCINER (*J. Pharm.* [5], **20**, 390—392).—A test solution, prepared by dissolving 1 gram of potassium perrutheniate in 20 c.c. of pure concentrated sulphuric acid, gives the following reactions:—With *solanine*, the liquid slowly becomes red, the colour disappearing at a gentle heat. *Ononine* becomes reddish-brown immediately. *Chelidonine* gives a green coloration; with potassium sulphoniobate, this same alkaloïd becomes brownish-red. *Imperatorine*, obtained by Ossan from *Imperatoria ostruthium*, gives with the test solution a blue coloration which quickly becomes intense green. This reaction is very delicate with

the perrutheniate, although the other alkaloïds give the best results with the rutheniate.

Freshly prepared ammonium sulphouranate (1 gram of ammonium uranate in 20 c.c. of concentrated sulphuric acid) gives with *codeïne* a blue coloration on gently heating; *imperatorine* gives a blue coloration which quickly disappears on heating; *morphine* gives a dirty-green on gently heating; and *chelidonine* slowly affords a green coloration. J. T.

Colouring Matter of Wines. By MONNET (*Bull. Soc. Chim.* [3], **2**, 144).—In contradistinction to the other metallic sulphides which remove the colouring matter from wines, arsenic sulphide yields the colour up to unacidified alcohol, and the violet substance obtained on evaporation of the tincture is soluble in alcohol, glycerol, etherised water, and slightly less so in ordinary water.

The residue obtained on evaporating the tincture yielded by the arsenic sulphide precipitate to alcohol, acidified with acetic acid, is blue and partly soluble in alcohol; whilst that similarly obtained by means of lead sulphide is insoluble in alcohol, and is not the normal colouring matter of wine, as it was deemed to be by Mülder and Maumené. T. G. N.

Detection of Alkanna Red in Wine. By J. HERZ (*Zeit. anal. Chem.*, **28**, 637).—Alkanna red is very easily taken up from its solutions by amyl alcohol. On adding to the amyl alcohol solutions a few drops of olive oil or oil of almonds, and evaporating off the alcohol on the water-bath, the oily residue (after washing with water) has a fine red colour, which, on saponification, becomes a rich blue, or, if the alkanna used was old, a green. M. J. S.

Valuation of Indigo. By M. HÖNIG (*Zeit. ang. Chem.*, 1889, 280—283).—The reduction and oxidation methods for estimating the indigotin in indigo give results which are respectively much below and above the truth. The author prefers to weigh the indigotin after extraction with boiling aniline or nitrobenzene. For this purpose, about 0·5 to 0·8 gram of the indigo, finely powdered and dried at 100—110°, is well mixed with three or four times its bulk of ignited pumice in grains of about a cubic millimetre. The mixture is introduced into a small Zulkowski-Wolfbauer percolation apparatus, which is connected with an upright condenser and a flask containing 50 c.c. of dry aniline. On boiling the aniline the vapours pass to the upper part of the percolator, and, condensing, fall while hot upon the mixture. It is essential to a rapid extraction that the aniline should percolate through the mixture while as hot as possible; hence the necessity for avoiding the presence of pumice dust. When the extract no longer runs off blue, the apparatus is cooled, and the aniline adhering to the pumice is displaced by 95 per cent. alcohol, which is collected apart. The extracted mixture should be dried, broken down, and returned to the percolator, to be once more extracted with the aniline. The aniline solution is then concentrated to about 10 c.c., and after cooling is measured in order to make a correction of 1·3 milligrams per

c.c. (2·1 milligrams if nitrobenzene has been used) for the solubility of indigotin in the cold. It is then mixed with five or six volumes of alcohol (that which had been used for washing the pumice), and the indigotin is collected on a tared filter, washed with alcohol as long as the washings have a brown colour, dried at 110°, and weighed. It is well to determine any ash it may contain, as particles of pumice may have passed through the plug of cotton-wool placed at the bottom of the percolator. M. J. S.

Lime in Tanning Materials. By M. PETROWITSCH (*Zeit. anal. Chem.*, **28**, 606—607).—In examining tanning materials, it is not usual to do more than determine the tannin, as they are rarely adulterated. The author has met with a specimen of valonia, which, when used for tanning, produced bluish-black stains, such as might be attributed to the presence of lime. The ash amounted to 6·36 per cent., which is $2\frac{1}{2}$ times as much as in pure valonia; and the lime constituted 6·37 per cent. of the ash, being about twice as much as it should have been. From the sample there was easily picked out 0·815 per cent. of small pebbles, some of which were calcareous.

M. J. S.

Trichloracetic Acid as a Reagent for Albumin. By BOYMOND (*J. Pharm.* [5], **20**, 482—484).—Marsanlt, Languepin, and Patein have indicated the existence in some urines of a variety of albumin which is coagulated by heat, but which is redissolved by acetic acid. Trichloracetic acid precipitates this variety of albumin, and the author recommends the substitution of this acid for nitric acid in a process given by Patein for the examination of urine, in which the globulin is determined by the aid of magnesium sulphate, the sereïn (? serum albumin) in a second portion by boiling with the addition of a few drops of acetic acid, and in the filtrate from this portion, the new variety is precipitated by the addition of nitric acid and boiling.

J. T.

Determination of Caseïn. By H. AURIOL and D. MONNIER (*Chem. Centr.*, 1889, ii, 521; from *Arch. sci. phys. nat. Genève*, **22**, 55—58).—Caseïn is precipitated by copper sulphate, the copper caseate being insoluble in excess of the reagent, whereas the analogous precipitates obtained with albumin and proteïn substances are soluble in excess of copper sulphate, the only other exception being globulin. In applying this fact to the quantitative determination of caseïn, 1 or 2 c.c. of milk is precipitated with 5 c.c. of a 5 per cent. solution of copper sulphate, the mixture warmed on the water-bath, with constant stirring, and, after cooling, the precipitate is filtered, washed with distilled water, alcohol, and ether, and weighed; from this weight, the weight of the mineral matter carried down with it is deducted. The latter was found to be usually 10 per cent.

J. W. L.

General and Physical Chemistry.

Studies in Chemical Optics with Reference to the Dissociation Theory. By M. LE BLANC (*Zeit. physikal. Chem.*, **4**, 553—560).—The atomic refractions of the elements are subject to variations as yet unexplained, and hence in many cases, even when no double bond is present, the molecular refraction is not equal to the sum of the atomic refractions. Gladstone has already pointed out that in hydrogen chloride the hydrogen has apparently a greater refractive power than in hydrogen bromide, and the author finds that this is the case with other acids, the refractive power of hydrogen increasing with the dissociation of the acid, and hence decreasing with the concentration. The influence of dissociation on the refraction of salt solutions is also apparent, but is not of as definite a character.

H. C.

Spectra of Gases at Low Temperatures. By K. R. KOCH (*Ann. Phys. Chem.* [2], **38**, 213—216).—The author finds that down to a temperature of $-100°$ no change takes place in the spectra of air, oxygen, and hydrogen. Hence he concludes that the spectrum of the *Aurora Borealis* is not merely that of air at low temperature, since the lines in the first are of far greater intensity than those of the latter.

H. C.

Circular Polarisation of certain Tartrate Solutions. By J. LONG (*Amer. J. Sci.* [3], **38**, 264—276; compare Abstr., 1889, 380).—The author has continued his investigation of the influence of inactive salts on the optical rotation of many tartrate solutions.

Potassium Antimony Tartrate.—The rotatory power decreases with rise of temperature, but increases with the concentration of the solution; at 20° with a 2 per cent. solution $[\alpha] = 140·7°$, and with a 5 per cent. solution $[\alpha] = 141·4°$. It is reduced by addition of chlorides, nitrates, or acetates of ammonium or sodium, the effect increasing in the order given.

Thallium Tartrate, $2Tl_2C_4H_4O_6 + H_2O$.—In a 5 per cent. solution at 20° $[\alpha] = 4·758°$, but the rotatory power increases with the temperature. It is also increased by addition of sodium and potassium salts, the effect being greatest in the case of potassium carbonate; doubtless owing to the formation of some potassium tartrate.

Thallium hydrogen tartrate, $HTlH_4C_4O_6$, in a 1 per cent. solution at 20° has a rotatory power $[\alpha] = 12·02°$.

Thallium Sodium Tartrate, $TlNaH_4C_4O_6 + 4H_2O$.—The rotatory power decreases with the concentration; in a 5 per cent. solution of the hydrated salt at 20°, $[\alpha] = 9·065°$, in a 20 per cent. solution, $[\alpha] = 6·492°$. It increases, however, with the temperature; with a 10 per cent. solution of the anhydrous salt, $[\alpha] = 8·595°$ at 20°, and

9·490° at 28°. Sodium sulphate increases the rotatory power, but thallium sulphate reduces it.

Thallium Lithium Tartrate, $TlLiH_4C_4O_6 + H_2O$.—The rotatory power decreases rapidly with the concentration; in a 5 per cent. solution at 20°, $[\alpha] = 9·456°$, and in a 20 per cent. solution $[\alpha] = 6·693°$. Lithium salts increase the rotatory power, but thallium sulphate produces a marked reduction.

Thallium antimony tartrate, $TlSbOH_4C_4O_6 + H_2O$, is obtained in small crystals resembling the potassium salt by boiling antimony oxide with thallium hydrogen tartrate. The rotatory power decreases with the temperature; in a 2 per cent. solution, $[\alpha] = 100·443°$ at 20°, and 99·644° at 28°. The rotatory power is reduced by inactive salts, especially acetates.

Thallium Potassium Tartrate, $TlKC_4H_4O_6$.—The rotatory power decreases with the concentration, but increases with the temperature; in a 5 per cent. solution at 20°, $[\alpha] = 10·057°$, in a 20 per cent. solution, $[\alpha] = 8·173°$; in a 10 per cent. solution, $[\alpha] = 8·840°$ at 20°, and 10·072° at 30°. Potassium and sodium salts increase the rotatory power; thallium salts reduce it.

Thallium Ammonium Tartrate, $TlNH_4C_4H_4O_6$.—The rotatory power decreases with the concentration, but the increase with the temperature is more rapid than in the case of the potassium salt; in a 5 per cent. solution at 20°, $[\alpha] = 10·032°$, in a 20 per cent. solution, $[\alpha] = 7·563°$.

Potassium Boro-tartrate, $KBOC_4H_4O_6$.—This salt retains water over sulphuric acid, and was, therefore, dried at 100°. The rotatory power increases markedly with the concentration, but decreases with the temperature; in a 5 per cent. solution at 20°, $[\alpha] = 58·101°$, in a 20 per cent. solution, $[\alpha] = 68·287°$; with a 10 per cent. solution, $[\alpha] = 59·055°$ at 20°, and 57·286° at 29°. Inactive salts and boric acid produce a considerable increase in the rotation, a result which is unexpected, because the rotatory power of the sodium and potassium salts is lower than that of the boro-tartrate. It seems that boric acid is liberated in the manner indicated by the equation $KBOC_4H_4O_6 + NaCl + 2H_2O = KNaC_4H_6O_4 + H_3BO_3 + HCl$, a supposition confirmed by the taste and reaction of the solution, and by the fact that a mixture of sodium potassium tartrate, boric acid, and hydrochloric acid has practically the same rotatory power. Boric acid probably acts on the alkaline tartrates forming complex compounds of high rotatory power analogous to those described by Gernez.

The effect of inactive salts is probably due to partial interchange of the bases, and observations of the rotatory power should afford evidence of the extent of such changes. Mixtures of the alkaline acetates and the antimony tartrates which show such a marked reduction in rotatory power are in a state of unstable equilibrium, and readily form precipitates after some time, or if heated. The optical properties of solutions in unstable equilibrium seem worthy of further investigation. C. H. B.

Theory of the Voltaic Cell and of Galvanic Polarisation. By E. WARBURG (*Ann. Phys. Chem.* [2], **38**, 321—344).—The author

regards the polarisation of the electrodes and change in the E.M.F. of voltaic cells as being in great measure caused by the presence of absorbed air. Cells consisting of electrodes of the same metal in one and the same electrolyte, the air contained in which, however, varied at the two electrodes, were constructed and examined. Such cells the author terms air cells.

Air cells, the electrolyte of which is a salt of the metal forming the electrodes, have an E.M.F. which is small and decreases with the concentration of the electrolyte. With mercury electrodes, and some chloride as electrolyte, the E.M.F. is small; with a sulphate as electrolyte, the E.M.F. is very much greater. The author regards these air cells as a special form of Grove's gas battery, the active gas being oxygen. The oxygen combines with the metal of the electrode, some of which dissolves in the electrolyte, thus bringing about a difference in concentration at the two electrodes and causing a concentration current. This effect will of course be more marked in dilute than in concentrated solutions, and with mercury less in the case of chlorides than in that of sulphates, as the mercury is more readily dissolved by the latter. It is shown that when mercury is agitated in contact with a magnesium sulphate solution containing absorbed air, oxide is formed on the surface and some of it goes into solution.

This behaviour of air cells will of course be common to all other voltaic cells. Each electrode will become surrounded by a weak solution of a salt of its own metal, and the differences in concentration will cause a change in the E.M.F. of the cell. Hence a portion of the so-called polarisation current may be simply a concentration current.

H. C.

Measurement of the Internal Resistance of Batteries. By B. O. PEIRCE and R. W. WILLSON (*Amer. J. Sci* [3], **38**, 465—468). —The method of alternating currents did not give satisfactory results when the poles of the battery were connected with a conductor of moderate resistance for an interval of less than $\frac{1}{10000}$ of a second, it being assumed that the E.M.F. of the battery was the same during this short interval as it was immediately before when the circuit was open. By means of a special apparatus, the poles of the battery could be connected with shunts of various resistances for any interval of time between 0·3 and 0·0001 of a second, and during this interval a condenser of suitable capacity was charged by connecting its poles with the poles of the battery, and then disconnecting them. The charge received by the condenser was afterwards measured by means of a ballistic galvanometer. No signs of fatigue in the battery were observed, and the results were the same whether the battery was shunted for 0·5 or 0·001 of a second. The values for the internal resistances of various cells measured in this way were always greater than the values obtained by the method of alternating currents, and in most cases there is a tendency for the internal resistance to decrease as the strength of the current which the cell is delivering increases.

C. H. B.

Theory of the Secondary Cell. By F. STREINTZ (*Ann. Phys. Chem.* [2], **38**, 344—362).—The author, in conjunction with Aulinger

(*Ann. Phys. Chem.* [2], **27**, 178), formerly advanced the theory that the hydrogen plate is the seat of the decrease of the E.M.F. of the secondary cell; this is shown to be the case in the present paper by experiments on the charging and discharging of secondary cells, during discharge, the potential of the positive plate remaining practically constant and of a value to which that of the negative plate gradually approximates. In cells containing two negative plates and only one positive plate, each negative plate may be discharged and the potential brought to that of the positive plate, while the latter remains practically unaltered. In fact, the durability of the positive, in comparison with that of the negative plate, is very great.

The study of the effect of current density on the potential differences led to the discovery that lead has, in a very marked degree, the power of occluding hydrogen, the occlusion being apparently similar in character to that observed in palladium. H. C.

Maximum Polarisation of Platinum Electrodes in Sulphuric Acid. By C. FROMME (*Ann. Phys. Chem.* [2], **38**, 362—395).—In a former paper (Abstr., 1888, 390), the author has described experiments on the polarisation of platinum electrodes in sulphuric acid, and in continuation of this work he has now examined the polarisation of platinised platinum electrodes. The change in the amount of polarisation with the concentration of the acid was formerly found to take place in a most complicated manner, several maxima and minima occurring on the curve representing this change. With platinised electrodes, this is not the case; the change is found to be a very regular one, and the polarisation is almost independent of concentration. If the cathode alone be platinised, the change is also perfectly regular, but in this case the polarisation increases with the concentration. With only the anode platinised, however, irregularities are still observed in the polarisation in dilute solutions, but in concentrated solutions (from 20 per cent. acid) the polarisation is small and practically constant. This is explained by the fact that the platinising of the cathode decreases the polarisation in a dilute, but has very little effect in a concentrated solution, whereas platinising the anode very considerably decreases the polarisation in concentrated, and exercises practically no influence on dilute solutions. Hence the maxima of polarisation formerly observed with non-platinised electrodes are due to the cathode in dilute solutions, and to the anode in concentrated solutions, and when both electrodes are platinised these no longer occur. It would seem that the platinising of the cathode assists the formation of gas bubbles in the dilute acids, and the formation of secondary products, such as persulphuric acid and hydrogen peroxide, takes place at the anode with greater readiness when not platinised.

The above effects with platinised electrodes cannot be obtained by merely increasing the size of those formerly used. The maximum of polarisation is reached in a very much shorter time by platinised than by the other electrodes. With a platinised cathode in dilute solution, or a platinised anode in concentrated solution, the polarisation is found to be independent of the strength of the current. H. C.

Transfer of Ions in Fused and Solid Silver Iodide. By O. LEHMANN (*Ann. Phys. Chem.* [2], **38**, 396—402).—A microscopical examination of the behaviour of silver iodide on electrolysis, in which various cases are distinguished and minutely described. H. C.

Resistance of Electrolytic Cells. By H. R. SANKEY (*Proc. Roy. Soc.*, **45**, 541—543).—The author has examined the increase of resistance with decrease of current density in electrolytic cells, known as "transfer" resistance. A current of 2·7 milliampères was gradually increased up to 370 milliampères, with the result that as the current increased the resistance diminished, rapidly at first, afterwards more slowly. The current was now again decreased to 2·7 milliampères, when the resistance became smaller, but immediately began to rise. The current was now increased as before, with the result that the resistance again diminished, but more slowly than before. When the current had again reached 370 milliampères, the resistance was practically the same as on the first occasion, and the transfer resistance was small. The author considers that the "transfer" resistance is not due to a non-conducting layer formed on one or both electrodes, since, in this case, the resistance should increase as the current increases, and should be greater after the application of a strong current than before, but that it may be due to a molecular interaction at the junction of the electrodes with the electrolyte offering a greater resistance to weak currents than to strong. With weak currents, the "transfer" resistance diminished very rapidly as the temperature increased, becoming very small at 70°. H. K. T.

Electrolysis of Mixed Solutions. By O. LEHMANN (*Zeit. physikal. Chem.*, **4**, 525—531).—The author has examined microscopically the separation of two metals from their mixed solutions on electrolysis, in order to ascertain whether the metals would simply separate out side by side, form mixed crystals, or enter into chemical combination to form an alloy of definite crystalline structure and physical properties. From mixtures of zinc and stannous chlorides and cadmium and stannous chlorides, the metals appear to separate out side by side. The appearance of the separated metals in the first case seems to warrant the assumption that tin is more readily deposited on a tin, and zinc more readily on a zinc electrode. From a mixture of silver and mercury nitrates, silver and mercury are deposited separately, but some amalgam is also formed. H. C.

Voltaic Energy of Dissolved Chemical Compounds. By G. GORE (*Proc. Roy. Soc.*, **45**, 442).—The author has examined the voltaic energy of nearly 250 different solutions of salts by means of the voltaic balance (compare Abstr., 1889, 665). The solutions examined comprise compounds of elements with elements, elements with mono-, bi-, and tri-basic acids; acids of these three classes with each other; elements with mono-, bi-, and tri-basic salts; mono-, bi-, and tri-basic acids with all these classes of salts, and all these salts with one another. The general results of the investigation prove that "every electrolytic substance or mixture when dissolved in water

unites chemically in definite proportions by weight with every other such dissolved body." The present research has discovered nearly 250 such compounds. H. K. T.

Dilatation of Salt Solutions. By N. A. TCHERNAY (*J. Russ. Chem. Soc.*, **21**, 176—183; compare Abstr., 1889, 204, 330, 1101). The following table gives the dilatation of solutions of the chlorides:—

HCl	+ 50H_2O	$v_t = 1$ +	$0{\cdot}0000652t$	+	$0{\cdot}000004355t^2$
LiCl	+ 50H_2O	$v_t = 1$ +	$557t$	+	$4036t^2$
NH_4Cl	+ 50H_2O	$v_t = 1$ +	$746t$	+	$3997t^2$
NaCl	+ 100H_2O	$v_t = 1$ +	$602t$	+	$4825t^2$
KCl	+ 100H_2O	$v_t = 1$ +	$590t$	+	$4407t^2$
$MgCl_2$	+ 100H_2O	$v_t = 1$ +	$688t$	+	$3922t^2$
HCl	+ 25H_2O	$v_t = 1$ +	$0{\cdot}0001515t$	+	$3209t^2$
NN_4Cl	+ 25H_2O	$v_t = 1$ +	$1407t$	+	$3649t^2$
NaCl	+ 50H_2O	$v_t = 1$ +	$1457t$	+	$3758t^2$
KCl	+ 50H_2O	$v_t = 1$ +	$1239t$	+	$3611t^2$
RbCl	+ 50H_2O	$v_t = 1$ +	$1267t$	+	$3716t^2$
$MgCl_2$	+ 50H_2O	$v_t = 1$ +	$1394t$	+	$2892t^2$
$CaCl_3$	+ 100H_2O	$v_t = 1$ +	$1085t$	+	$3613t^2$
$BaCl_2$	+ 100H_2O	$v_t = 1$ +	$1345t$	+	$3537t^2$
HCl	+ 12·5H_2O	$v_t = 1$ +	$2800t$	+	$1650t^2$
NaCl	+ 25H_2O	$v_t = 1$ +	$2573t$	+	$2393t^2$
KCl	+ 24·7H_2O	$v_t = 1$ +	$2141t$	+	$2588t^2$
$MgCl_2$	+ 25H_2O	$v_t = 1$ +	$1941t$	+	$1856t^2$
$CaCl_2$	+ 50H_2O	$v_t = 1$ +	$1925t$	+	$2647t^2$
$SrCl_2$	+ 50H_2O	$v_t = 1$ +	$2204t$	+	$2542t^2$
$BaCl_2$	+ 50H_2O	$v_t = 1$ +	$2393t$	+	$2456t^2$
HCl	+ 6·25H_2O	$v_t = 1$ +	$4460t$	+	$2125t^2$
NaCl	+ 12·5H_2O	$v_t = 1$ +	$3640t$	+	$1237t^2$

Here, as in the case of nitrates, some of the solutions exhibit an analogous dilatation by heat, although the relation of the number of salt-molecules to that of the water-molecules is not the same; for example, potassium and sodium chlorides with 100H_2O, and lithium and ammonium chlorides with 50H_2O, show the same dilatation.

The same regularity is observed in the case of the dilatation coefficients (δ), the increment of the coefficient with increasing temperature being larger for KCl and NaCl solutions than for solutions of HCl, LiCl, and NH_4Cl, even in the case of different concentrations. This shows that the physical and chemical processes (dissociation) follow different laws for each group of solutions, so that the molecular constitution of the salt hydrates of both groups must be different. The values are:—

NaCl	+ 100	H_2O δ =	0·0000602	+	$0{\cdot}0000096t$
KCl	+ 100	H_2O δ =	590	+	$88t$
HCl	+ 50	H_2O δ =	652	+	$87t$
LiCl	+ 50	H_2O δ =	557	+	$81t$
NH_4Cl	+ 50	H_2O δ =	746	+	$79t$

NaCl	+ 50 H_2O	δ =	0·0001457 +	0·0000075t
KCl	+ 50 H_2O	δ =	1239 +	72t
HCl	+ 25 H_2O	δ =	1515 +	64t
NH_4Cl	+ 25 H_2O	δ =	1407 +	61t
NaCl	+ 25 H_2O	δ =	2573 +	47t
KCl	+ 24·7 H_2O	δ =	2157 +	48t
HCl	+ 12·5 H_2O	δ =	2800 +	33t
NaCl	+ 12·5 H_2O	δ =	3640 +	24t
HCl	+ 6·25 H_2O	δ =	4460 +	04t

A similar relation is found to hold in the case of the dilatation coefficients of $CaCl_2$, $SrCl_2$, $BaCl_2$ solutions on the one hand, and those of $MgCl_2$ on the other, the first showing a dilatation analogous to that of a solution of $MgCl_2$ containing only half the amount of water-molecules, and the increment of dilatation with rising temperature is smaller for $MgCl_2$ solutions than for those of $CaCl_2$, $SrCl_2$, $BaCl_2$ solutions, thus :—

$CaCl_2$	+ 50H_2O	δ =	0·0001925 +	0·0000053t
$SrCl_2$	+ 50H_2O	δ =	2204 +	51t
$BaCl_2$	+ 50H_2O	δ =	2393 +	49t
$MgCl_2$	+ 25H_2O	δ =	1941 +	37t
$SrCl_2$	+ 100H_2O	δ =	1085 +	72t
$BaCl_2$	+ 100H_2O	δ =	1345 +	71t
$MgCl_2$	+ 50H_2O	δ =	1394 +	56t

There are two types of salt solution : the one expanding more, the other less, in the same molecular concentration. To the first type belong the chlorides of Na, K, Rb, Ca, Sr, Ba ; to the second type those of H, Li, NH_4, and Mg. Supposing that the dilatation depends on the relation between the salt-molecules and the water-molecules, the author concludes that the solutions of the second type contain only half the number of molecules that those of the first type do. The molecules of $MgCl_2$ in solution are therefore at least Mg_2Cl_4 derived from the type H_4Cl_4, those of $CaCl_2$ being simple and derived from H_2Cl_2. But as the solutions of $MgCl_2$, HCl, LiCl, and NH_4Cl show an analogous dilatation, they must all correspond with the type H_4Cl_4 ; whilst, for the same reason, those of $CaCl_2$, KCl, NaCl must belong to the type H_2Cl_2. There may be some relation between this and J. Thomsen's hypothesis that the solution of hydrogen chloride contains $H_2Cl·OH$. B. B.

Heat of Formation of Potassammonium and Sodammonium. By JOANNIS (*Compt. rend.*, **109**, 965—967).—The compounds (this vol., p. 209) were formed in a glass vessel which could be closed by a stopcock, and the vessel was immersed in the calorimeter and the stopcock opened. The compound dissociated, and the ammonia escaped through a serpentine tube also immersed in the calorimeter. The quantity of heat absorbed under these conditions is equal to the heat of formation of the compounds from the alkali metal and gaseous ammonia at atmospheric pressure.

NH_3 gas + Na solid = NH_3Na solid...... develops +5·2 Cals.
NH_3 liquid + Na solid = NH_3Na solid.... „ +0·8 „

NH_3 gas + K solid = NH_3K solid........ develops +6·3 Cals.
NH_3 liquid + K solid = NH_3K solid...... „ +1·9 „

It is evident that when these compounds take part in reactions, and the ammonia escapes without producing secondary changes, the effect will be practically the same as that of the alkali metal alone; but if the ammonia takes part in the reaction, these derived ammonias will act more energetically than the sodium or potassium which they contain. C. H. B.

Thermochemical Data respecting Succinic and Isosuccinic Acids. By S. TANATAR (*J. Russ. Chem. Soc.*, **21**, 183—188).—The thermochemical data obtained by the author give, in combination with other data obtained by previous investigators, the following results:—

Heat of formation of potassium and sodium succinates—

$$C_4H_6O_4 \text{ (solid)} + 2KOH \text{ (solid)} = C_4H_4K_2O_4 \text{ (solid)} + 2H_2O \text{ (solid)} + 45{,}215 \text{ cal.}$$

$$C_4H_6O_4 \text{ (solid)} + 2NaOH \text{ (solid)} = C_4H_4Na_2O_4 \text{ (solid)} + 2H_2O \text{ (solid)} + 38{,}483 \text{ cal.}$$

The heat of formation of sodium isosuccinate—

$$C_4H_6O_4 \text{ (solid)} + 2NaOH \text{ (solid)} = C_4H_4Na_2O_4 \text{ (solid)} + 2H_2O \text{ (solid)} + 39{,}693 \text{ cal.}$$

In aqueous solution the heats of formation of the succinates are—

$$C_4H_6O_4 + 2KOH = 25{,}653 \text{ cal.};\ C_4H_6O_4 + 2NaOH = 25{,}506 \text{ cal.}$$

The corresponding values for the isosuccinates are—

$$C_4H_6O_4 + 2KOH = 27{,}354 \text{ cal.};\ C_4H_6O_4 + 2NaOH = 27{,}320 \text{ cal.}$$

It is seen that the formation of sodium isosuccinate from the acid and sodium hydroxide is accompanied by the development of more heat than the formation of sodium succinate, not only in solution, but also in the solid state.

The heat of dissolution of succinic acid at 9·5° is $C_4H_6O_4 + 400H_2O = -6{,}381$ cal. The corresponding value for isosuccinic acid at 12° is $C_4H_6O_4 + 200H_2O = -4{,}097$ cal. Similar relations are observed in case of fumaric and maleïc acids, and again with itaconic and citraconic acids. B. B.

Heat of Combustion of Isodibutylene and Isotributylene. By MALBOT (*Bull. Soc. Chim.* [3], **2**, 481—482).—On fractionating the product of the action of zinc chloride on isobutyl alcohol (Abstr., 1889, 842), isodibutylene and isotributylene, distilling respectively at 110—113° and 178—181° under a pressure of 768 mm., are ob-

tained. Their heats of combustion at 15° have the mean values: for isodibutylene 1252·5 cals., and for isotributylene 1858·9 cals.

T. G. N.

Relation of Volume, Pressure, and Temperature in the case of Liquids. By C. BARUS (*Amer. J. Sci.* [3], **38**, 407—408).—Experiments with alcohol, ether, paratoluidine, diphenylamine, paraffin, and thymol, and less complete experiments with other organic compounds, show that if temperature and pressure vary linearly at a mean rate of about 0·11° per atmosphere, there will be no change of volume. This holds good between 30° and 300°, and between 20 atmos. and 500 atmos., and therefore through a range of pressure six or seven times as large as that used by Ramsay and Young.

Other conditions being equal, the pressure necessary to solidify a substance is decidedly in excess of the pressure at which it liquefies again. The author has investigated this as a typical "lag" phenomenon, and has obtained data relating to paraffin, naphthalene, and palmitic and chloracetic acids.

At 185°, under a pressure of 20 atmos., water attacks lead glass so rapidly that in very fine capillary tubes the contents became opaque and solid in about an hour. During this action the compressibility of the water at 185° increased gradually and regularly to about three times its original value, and the isothermal volume of the silicated water decreased at least 13 per cent of the original volume.

In the case of mercury, the decrease in electrical resistance r and volume v through increased pressure between 0 and 400 atmos. were found to be proportional to each other.

C. H. B.

New Method of Determining Gas Densities. By J. P. COOKE (*Amer. Chem. J.*, **11**, 509—541).—The gases are weighed in a glass balloon of about 5 litres capacity and 570 grams weight. This is provided with two tubes, one reaching to the bottom of the balloon, the other attached to the top of its neck; these tubes are fitted with well-ground stopcocks. The balloon is filled with gas by placing it in a calorimeter, a thermometer in which indicates the same temperature as another placed in the external air, and passing into it a current of gas purified by passing successively through solutions of potash and of baryta, then up two long tubes placed at a slight inclination to the horizontal and containing strong sulphuric acid, and finally through two vessels containing phosphoric anhydride; a second vessel of phosphoric anhydride was found to be necessary, as the anhydride in the first became granular after a time, and failed to remove the last traces of moisture from the gas. In the case of carbonic anhydride, the potash and baryta solutions are of course dispensed with. In weighing the balloon, it was supended from one pan of a balance, and from the other was hung as a counterpoise another balloon of exactly equal volume. The wires by which these are suspended pass through holes in the floor of the balance-case, and the balloons hang in a sheet-metal chamber beneath, and are weighed only when a thermometer inside this chamber indicates the same

temperature as another thermometer placed in the external air. Temperature readings were accurate to 0·01°, barometer readings to 0·1 mm.

The first thing was to ascertain the tare of the empty balloon. This was first done by a modification of Regnault's method. The balloon was filled with hydrogen, and then exhausted to a known pressure (1·40 mm.) and weighed. This weight, when corrected for the weight of residual hydrogen and for the contraction of volume consequent on exhausting the globe, gives the tare of the empty balloon. This tare was then ascertained by the following "chemical method." The balloon was filled with carbonic anhydride and weighed. One of the stopcocks was then opened, and the gas sucked, by means of a Bunsen pump, through the following series of absorbing vessels: a bulb containing potash soluion, a U-tube containing soda-lime, a U-tube containing phosphoric anhydride, a third U-tube containing glass beads with a few drops of strong sulphuric acid to indicate any sucking back (this tube was not weighed), and lastly a bulb containing 50 c.c. of normal barium hydroxide solution. Finally by opening the second stopcock, a current of air was drawn through the purifying apparatus, in order to sweep all the rest of the carbonic anhydride out of the balloon into the absorbing vessels. The potash bulb, soda-lime tube, and phosphoric anhydride tube were weighed separately before and after the experiment, and the amount of baryta-water neutralised was determined by titration with oxalic acid; elaborate corrections were also made to reduce the weighings to a vacuum. The total gain in weight gives the weight of carbonic anhydride contained in the balloon, and this, when subtracted from the weight of the balloon when full of carbonic anhydride, gives the tare of the empty balloon. This was found to be 2·5573 by Regnault's, 2·55703 by the chemical method, each number being the mean of three closely agreeing experiments.

The balloon was now filled with purified air and with hydrogen at the atmospheric temperature and pressure, and its weight ascertained, three experiments being made in each case; its weight when full of carbonic anhydride is already known. (The hydrogen was obtained from an electrolytic generator, the carbonic anhydride from marble and hydrochloric acid.) By subtracting from these weights the tare of the empty balloon, the weights of the different gases which fill the globe are ascertained, and from these numbers the density of hydrogen was calculated to be 0·06958 using Regnault's, and 0·06962 using the chemical method of determining the tare, the density of air being taken as unity. For carbonic anhydride the density is 1·52856 (air = 1), or 21·971 (hydrogen = 1) by Regnault's method, and by the chemical method 1·52854 or 21·957 respectively. And further, using Regnault's number (1·10562) for the density of oxygen referred to air, and his own numbers for hydrogen, the author calculates, as the mean of three experiments, that the density of oxygen (hydrogen = 1) is 15·891 by Regnault's, or 15·882 by the chemical method. Lord Rayleigh obtained the number 15·884.

The author regards his results as showing that the atomic weight of oxygen (H = 1) is decidedly less than 16. He points out that, as

compared with hydrogen, the density of oxygen is slightly, and that of carbonic anhydride considerably greater than the halves of their respective molecular weights, and this is what one would expect, having regard to the fact that at the atmospheric temperature oxygen is considerably, and carbon anhydride very much nearer its critical point than hydrogen is at that temperature. Finally, the author expresses his approval of the provisional system of atomic weights which assumes $O = 16$ as its basis. C. F. B.

Formulæ for Calculating the Molecular Volumes of Organic Compounds. By W. LOSSEN (*Annalen*, **254**, 42—83).—The molecular volume of a compound $C_nH_mO_p$ if of the fatty series is given by the formula $10{\cdot}45n + 5{\cdot}225m + 10{\cdot}45p \pm \frac{1}{4}(n-2)^2 \pm 1{\cdot}5\mu$, if of the aromatic series by $10{\cdot}45n + 5{\cdot}225m + 10{\cdot}45p + \frac{1}{4}(n-4)^2 \pm 1{\cdot}5\mu$, where μ denotes the number of hydrogen-atoms necessary to convert an unsaturated into a saturated compound. With the aid of these formulæ, the author has calculated the molecular volumes of 407 organic compounds, and in only 97 cases or 24 per cent. are the calculated within 2 per cent. of the observed values. The author therefore concludes that it is impossible, taking account of every known influence, to express the molecular volume by any general formula that shall serve for all compounds. Results which are in good agreement with the observed may however be obtained from the expressions $(10{\cdot}24 \pm x0{\cdot}5)(n + p) + (5{\cdot}12 \pm x0{\cdot}25)m \pm \frac{1}{4}(n-2)^2 + 1{\cdot}4\mu$, where x may vary between 0 and 1 for the different homologous series, but is constant for the members of one and the same series.

H. C.

Vapour-pressure of Aqueous Solutions. By R. EMDEN (*Ann. Phys. Chem.* [2], **38**, 447—453).—A reply to a paper by Tammann on the same same subject (Abstr., 1889, 668), in which the accuracy of the author's own experiments and of Babo's law is upheld.

H. C.

Determination of the Molecular Weight from Vapour-pressure Reductions. By E. BECKMANN (*Zeit. physikal. Chem.*, **4**, 532—552).—The author describes various modifications which he has made in the present methods for determining the reduction of the vapour pressure of a solution by any dissolved substance, with the view of making this method of determining molecular weights of general use in the laboratory. The chief of these are those introduced for the purpose of accurately determining the boiling points of solutions, and from the rise in the boiling point of the solvent the molecular weights of the dissolved substances. A thick platinum wire sealed into the bottom of the vessel serves to conduct the heat to the solution, and overcomes the difficulty arising from boiling with bumping. The bulb of the thermometer which must be placed in the liquid is surrounded with a layer of asbestos tied on with platinum wire, and in this way is effectually shielded from currents of superheated liquid, and gives a constant register of the temperature of the boiling solution. In order also to overcome as far as possible the effect of convection currents, the vessel is filled to about half the volume of the solution with glass beads. The vessel itself which

contains the solution is provided with three tubular necks, through one of which passes the thermometer, through the second the end of the condenser tube, whilst the third serves for the introduction of the substance the molecular weight of which is being determined.

The calculation of the results is similar to that employed in the case of the reduction of the freezing point. A gram-molecule of substance dissolved in 100 grams of the solvent will raise its boiling point through t degrees, so that if the number of grams of substance in 100 grams of the solvent necessary to raise the boiling point 1° be determined, and this multiplied by t, the molecular weight will be obtained. The number t may either be directly determined from observations with a substance of known molecular weight, or, according to Arrhenius, $t = 0{\cdot}02T^2/W$, where T is the boiling point in absolute temperature, and W the heat of vaporisation of 1 gram of the solvent. H. C.

Cryoscopic Method of Determining Molecular Weights. By J. F. Eykman (*Zeit. physikal. Chem.*, 4, 497—519).—The author has determined the molecular reductions of the freezing points of a number of organic solvents from observations with compounds of known molecular weight, the apparatus used being that previously described (Abstr., 1889, 336). The results are tabulated and given in curve form. From the molecular reduction, the latent heat of fusion is calculated by means of Van't Hoff's formula, a correction being applied for that portion of the solvent which by crystallisation is removed from the sphere of action of the osmotic pressure. The calculated latent heats of fusion and the corrected molecular reductions of the solvents used are as follows:—

	Latent heat of fusion.	Molecular reduction.
Diphenyl	29·4	79·4
Diphenylmethane	27·1	65·6
Phenol	26·9	72·0
Parabromophenol	22·9	98·0
Paracresol	27·1	69·6
Thymol	27·9	73·9
Cetyl alcohol	34·3	59·7
Chloral alcoholate	27·0	74·4
Anethoïl	27·9	61·2
Benzophenone	23·2	87·8
Phenylpropionic acid	24·8	82·6
Capric acid	40·6	44·7
Stearic acid	54·4	42·5
Stearin	47·3	49·2
Urethylane	48·5	43·0
Urethane	41·0	49·6
Acetoxime	41·4	52·9
Azobenzene	29·4	77·6
Paratoluidine	38·6	51·1

For diphenyl, thymol, azobenzene, and urethane the latent heats o

fusion were also directly determined, the numbers obtained being 28·5, 27·5, 29, and 40·8. H. C.

Dissociation of Substances in Solution. By D. MENDELÉEFF J. Russ. Chem, Soc., 21, 198—202).—Van't Hoff's highly interesting paper, "Lois de l'équilibre chimique dans l'état dilué gaseux ou dissous" (1886), has attracted general interest to those values of i which are found from the osmotic pressures, from the isotonic coefficients, from the freezing temperatures, and from the vapour-pressures of dilute solutions. Ostwald and Arrhenius have given a new method of determining the same value of i from the electric conductivity of weak solutions, but as soon as Arrhenius, Planck, and Ostwald, in 1888, attempted to explain the deviation of i from unity for electrolytes by the assumption that the compounds in solutions dissociate to free electrolytes, Mendeléeff began to doubt the correctness of this hypothesis, which assumes (1) that conducting solutions have a constitution different from that of non-conducting solutions; (2) that in solutions of the first kind the value of i is larger than the unit, on account of the presence of free ions, and (3) that in non-conducting solutions there is no such dissociation, and, therefore, $i = 1$.

The phenomena of dissolution are, in a great many cases, identical in both kinds of solutions, and the assumption of free ions is very different from the very probable and satisfactory explanation given by Clausius as to there being a certain degree of interchange of atoms between the molecules of dissolved substances. The author does not agree with the hypothesis of free ions, as, after a continued study of solutions, he considers the phenomena to be most satisfactorily explained by the assumption that dissociated systems always exist, not only of the dissolved compounds, but also of their definite liquid hydrates, similar to melted crystallohydrates ($CaCl_2,6H_2O$, for example), or of unstable hydrates like those of Wroblewski, Roozeboom, &c. (See Mendeléeff's work "On Solutions, &c., 1877.")

The assumption of dissociation and of a reciprocal decomposition of molecules of the hydrates formed in solution does, according to the author, satisfy the claims by which Arrhenius, Planck, and Ostwald are bound to assume free ions in solutions. The author shows, by the discussion of the depression of the freezing point, that differences in the value of i for different compounds may be explained without assuming free ions in solutions. He shows, first, that the molecular depression dm (d being the depression for 1 gram of a substance with the mol. wt. m, dissolved in 100 grams of water) of the anhydrous salt in weak solutions will be equal to the molecular depression of any hydrate of the same salt. Let a definite hydrate with nH_2O be assumed. The depression for 1 gram of the anhydrous salt being d, for 1 gram of the hydrate (d_n), it will be as many times smaller than d as m is smaller than $m + n\,18$ if the solution be a weak one, that is $d_n = \frac{dm}{m + n18}$. If the solution be concentrated, then for 1 gram of the hydrate in 100 grams of water, $d_n = \frac{dm}{m + n18} \div \left(1 - \frac{0\ 18n}{m + 18n}\right)$. In

dilute solutions the divisor $1 - \frac{0.18n}{m + 18n}$ will be nearly equal to 1, and, therefore, for such solutions, $d_n = \frac{dm}{m + 18n}$. The molecular depression of the hydrate will therefore be $= \frac{dm}{m + 18n}(m + 18n)$, or $= dm$, that is, equal to the molecular depression of the anhydrous salt. A dilute solution of the anhydrous salt (m) or that of the hydrate ($m + 18n$) will give the same i, for this is equal to the molecular depression divided by 18·5, as shown by Van't Hoff (*loc. cit.*, p. 24).

For $MgSO_4$ the isotonic coefficients, as well as the molecular depression, give $i = 1·04$, from which $dm = 1·04 \times 18·5 = 19·24$, and $d = 0·160°$. According to the formula $d_n = \frac{dm}{m + 18n}$, for the hydrate $MgSO_4 + 7H_2O$ ($n = 7$) $d_n = 0·078°$. De Coppet and Rüdorff have shown that the depression of such a solution is proportional to the amount of the heptahydrated (not anhydrous) salt dissolved, namely, 1 gram $= 0·072—0·073°$, which, calculated as above, gives $i = 0·96$. This number differs very little from the value 1·04, calculated for the depression 0·078°, or $i = 1$. The value of i is, within the limit of error, identical for weak solutions of both $MgSO_4$ and $MgSO_4,7H_2O$, and the same will be the case for $MgSO_4,10H_2O$.

As, for dilute solutions, the same value of i is obtained both for anhydrous and for hydrated salts, the author concludes that neither the determination of osmotic pressures, nor of isotonic coefficients, nor of the vapour-pressure of weak solutions, nor of the molecular depression, nor of the electrolytic conductivities, will show whether the value of i, obtained by means of them, refers to anhydrous compounds or to hydrates (or generally to compounds formed with the solvent).

These methods cannot show the degree of hydration of the substance dissolved in water, and they cannot contradict the hypothesis which assumes the existence of particular dissociated hydrates in aqueous solutions. If there is a possibility and need of explaining the variation of i by means of dissociation, it would be better, prior to assuming a dissociation of MX in solution to M + X, to inquire whether, in solutions of salts MX, the action of the water does not give rise to molecules MOH + HX, or whether the hydrates $MX(n + 1)H_2O$ may not dissociate into the hydrates $MOHmH_2O + HX(n-m)H_2O$, or directly the hydrates $MXnH_2O$ into separate molecules. Such an hypothesis, in connection with that of the interchange of atoms between molecules, explains sufficiently the identity of i, obtained by different methods, as well as its variation for different substances. Before going further than Van't Hoff, it is necessary to investigate exactly (1) how the value of i changes with varying concentration for compounds giving different values for i, and (2) whether the values of i remain far from integers (for example, for $CaCl_2$, $i = 2·5$, for alums, $i = 4·5$, &c.) for varying temperatures and concentrations.

B. B.

Supersaturated Solutions. By A. POTILITZIN (*J. Russ. Chem. Soc.*). See p. 333.

Rate of Chemical Change. By G. GORE (*Proc. Roy. Soc.*, **45**, 440—442).—This is a continuation of the author's experiments on the use of the voltaic balance for determining the rate of chemical change in solution (compare Abstr., 1889, 665). Two solutions were examined: one containing equivalent quantities of chlorine and potassium iodide, the other equivalent quantities of potassium chloride and iodine. The general results of the investigation are, that the first solution is very unstable and loses energy, partly while being mixed, and to a further extent after a time, the change not being complete after a lapse of six days at a temperature of 12°. The second solution is nearly, but not quite, stable, as it increases slightly in voltaic energy after a time. The two solutions ultimately acquire a composition represented by 0·23 part of potassium iodide, 74·49 parts of potassium chloride, 126·8 parts of iodine, and 0·0497 part of chlorine.

The rate of change did not seem to be affected by daylight, but two minutes' ebullition had as much effect in altering the composition of the first solution as an interval of six days at the ordinary temperature. With the first solution, the loss of energy on mixing is greater the greater the concentration of the constituents. The loss was also greater when the chlorine solution was added to the iodide solution than when the reverse order of mixing was adopted. The colours of the solutions were in accordance with the above observations, that of the first solution being light, and gradually becoming darker, that of the second undergoing no appreciable change.

The "voltaic balance" method can be used in measuring the rate of change in liquids already mixed. It is simpler and more sensitive than thermochemical or colorimetric methods, and can be used for colourless liquids. H. K. T.

Determination of Affinity Coefficients. By M. CONRAD and C. BRÜCKNER (*Zeit. physikal. Chem.*, **4**, 631—657; see this vol., p. 4).—The authors have studied the action of the alkyl oxides of sodium and potassium on the chlorides, bromides, and iodides of organic radicles. The relation between the coefficients obtained is found to depend on the nature of the alkyl oxide and of the halogen, but is independent of the metal. Thus, for the ethoxide of sodium or potassium the relations between the affinity coefficients, that of the propyl compound being in each case taken as unity, are as follows:—

	Propyl.	Ethyl.	Allyl.	Benzyl.
Cl.	1	—	65·70	126·5
Br	1	3·24	61·34	120·1
I	1	2·85	54·34	93·95

The coefficients of the other groups approach that of the propyl as the atomic weight of the halogen with which they are associated increases.

If, however, the action of the potassium salt be compared with that of the sodium salt, the former is found to have the greater activity, for, setting that of potassium ethoxide in each case at 100, that of sodium ethoxide becomes for allyl chloride 79·0, and for benzyl chloride 88·4.

The comparative activities of chlorine, bromine, and iodine, putting that of the iodide in each case as 1000, are shown by the following numbers:—

	Iodide.	Bromide.	Chloride.
Propyl	1000	473	7·63
Allyl	1000	532	9·23
Benzyl	1000	604	10·28

Methyl bromide shows an exceptional behaviour, and is found to have an activity greater than that of the iodide. H. C.

Increase in Chemical Energy at the Free Surface of Liquid Substances. By W. SPRING (*Zeit. physikal. Chem.*, 4, 658—662).—The author shows, by various experiments, that there exists at the free surface of any liquid a layer which possesses a superior chemical activity to that of the rest of the liquid. For instance, if a prism of calcspar be immersed to about half its length in hydrochloric acid, the action at the surface is so vigorous that in a short space of time the prism is cut in two, and the lower half sinks in the acid. No satisfactory explanation for these facts can be given. H. C.

Chemical Energy at the Surface of Liquids. By J. BECHHOLD (*Zeit. physikal. Chem.*, 5, 68).—The phenomena observed by Spring (preceding abstract) are explained by the author on the assumption that the liquid at the surface on dissolving some of the crystal becomes denser and sinks in the solution down the sides of the crystal, thus protecting the lower portion from the action of the solvent, and also making way for fresh quantities of the latter at the surface. If in the calcspar experiment the upper portion of the prism be coated with wax, and the whole then immersed vertically in the acid, the prism will now be cut in two at the boundary of the wax coating, although this is far below the surface of the liquid. H. C.

Isomorphism. By J. W. RETGERS (*Zeit. physikal. Chem.*, 4 593—630; compare Abstr., 1889, 931).—This paper contains a study of the isomorphism of the nitrates of the alkali metals and of silver by means of the specific gravities of the mixed salts. The nitrates of ammonium, potassium, thallium, and silver crystallise in the rhombic system, those of sodium, lithium, rubidium, and cæsium in the hexagonal system. Sodium and silver nitrates form an isodimorphou

series, hexagonal crystals being formed containing as much as 52·57 per cent. of silver nitrate, and rhombic crystals containing up to 0·8 per cent. of sodium nitrate from mixed solutions of the two salts. Isodimorphism is also observed with mixtures of the other nitrates, although not quite to as marked a degree as in the above example. The author concludes from this that, although a salt may crystallise in some stable form, it is capable of existing in an indefinite number of unstable modifications, and that polymorphism, far from being the exception, is probably the rule for all solid chemical substances. H. C.

Inorganic Chemistry.

Apparatus for Distillation under Reduced Pressure. By H. GAUTIER (*Bull. Soc. Chim.* [3], **2**, 675).—To the base of a wide glass tube, smaller tubes are fused in such a way that by the rotation on an upper accurately-ground tube carrying the delivery tube of the condenser, the latter may be successively approximated to their upper orifiees and several flasks be filled without vitiating the vacuum.

T. G. N.

Colour and Spectrum of Fluorine. By H. MOISSAN (*Compt. rend.*, **109**, 937—940).—Fluorine in small quantities seems to be colourless, but when examined in a platinum tube 50 cm. in length, with plane ends of colourless fluorspar, it is seen to have a distinct greenish-yellow colour, paler than that of chlorine and decidedly yellower. A column of the gas 1 metre in length shows no definite absorption bands.

If a small quantity of water is introduced into the tube containing the fluorine, it is decomposed with formation of hydrogen fluoride and ozone, the latter having the deep indigo-blue colour described by Hautefeuille and Chappuis.

Salet compared the spectra of silicon fluoride and silicon chloride and described the spectrum of fluorine as consisting of five lines in the red. The author employed a platinum tube closed by transparent stoppers of fluorspar and provided with sparking wires of platinum and of gold. He examined the spectra when the tube was filled with air and when it was filled with fluorine, making observations with both the gold and platinum electrodes, and he also examined the spectra of hydrogen fluoride, silicon fluoride, and phosphorus trifluoride. The lines common to all these spectra are regarded as the lines due to fluorine, and their wave-lengths are as follows:—*very faint*, 749, 740, 734; *faint*, 714, 704, 691, 687·5, 685·5, 683·5; *strong*, 677, 640·5, 634, 623. Salet gives the wave-lengths of two feeble lines as 692 and 686, and of three strong lines as 678, 640, 623.

The spark spectrum of hydrogen fluoride contains several very broad and indistinct bands in the orange and the violet, but their wave-lengths could not be determined. C. H. B.

Formation of Ozone during Rapid Combustion. By O. LOEW (*Ber.*, **22**, 3325—3326).—Ilosvay comes to the conclusion (*Bull. Soc. Chim.* [3], **2**, 360—377) that ozone is never formed during rapid combustion. The author has clearly obtained the odour of ozone when a rapid current of air was blown across the upper part of a flame. This is especially noticeable with a Bunsen burner. Thann and Schnauss have made similar observations (*Jahresb.*, 1870).

L. T. T.

Composition of Water. By LORD RAYLEIGH (*Proc. Roy. Soc.*, **45**, 425—430).—This paper is a continuation of the author's researches on the relative densities of hydrogen and oxygen (compare Abstr., 1888, 643). Various attempts were made to obtain lighter hydrogen than hitherto, especially by means of aluminium in alkaline solution, but without success. The gas was also purified by absorption with palladium so as to free it from nitrogen, but the hydrogen was no lighter than before. In the author's previous researches, the composition of water was determined by combining the ratio of densities with that found by Scott (Abstr., 1888, 411) for combination by volume. In this paper, experiments are described in which the combining proportions are determined by direct weighing. The gases were weighed in glass globes, from which they were exhausted by means of Sprengel pumps, first into a mixing chamber and thence into a eudiometer. The manipulative difficulties were very great, owing to the necessity of maintaining the gases in approximately equivalent proportions. When sufficient quantities of the gases had been pumped out, the flasks were again weighed, the (calculated) weight of the residual gas (generally oxygen) in the eudiometer being deducted from the weight of the gas taken. A mean of five experiments gave 15·89 as the atomic weight of oxygen after allowing for the effect of pressure on the glass globes (*loc. cit.*). This result is somewhat lower than the value (15·91) obtained from the relative densities of hydrogen and oxygen and Scott's combining ratio by volume. The residual gas (from 2000 c.c. of mixed gases) was analysed, and was found to contain 0·1 c.c. of nitrogen and 0·05 c.c. of carbonic anhydride. As these gases were probably contained in the oxygen, their effect is negligible. The water of combustion was examined for nitric acid with negative results. H. K. T.

Thiosulphates. By A. FOCK and K. KLÜSS (*Ber.*, **22**, 3310—3316; compare this vol., p. 210).—The authors have prepared the following thiosulphates:—$Sr_2S_2O_3 + H_2O$, $MgS_2O_3 + 6H_2O$, $NiS_2O_3 + 6H_2O$, $CoS_2O_3 + 6H_2O$, and $Fe_2S_2O_3 + 5H_2O$; the crystal measurements of the salts are given. F. S. K.

Preparation of Nitrogen. By BERTHELOT (*Bull. Soc. Chim.* [3] **2**, 643—645).—Nitrogen obtained by the action of copper and ammonia solution on air is always contaminated by ammonia and traces of nitrite, which are best removed by passing the gas first through aqueous potash and then through sulphuric acid, the final traces of oxygen being absorbed by chromous chloride solution. The usual order is thus reversed, because sulphuric acid decomposes th

nitrite to form traces of nitrogen dioxide, which are not absorbed by the potash. T. G. N.

Freezing Points of Arsenic Chloride and Stannic Chloride. By BESSON (*Compt. rend.*, **109**, 940—941).—Arsenic trichloride carefully purified from excess of chlorine solidifies at −18° with very considerable contraction, and crystallises in white, nacreous needles. If, however, the chloride is saturated with chlorine at 0°, the product does not solidify above −30°, but at this temperature it freezes with very great contraction. At −30° the arsenic chloride will absorb a much larger quantity of chlorine, yielding a yellow liquid which does not solidify at −60°. If this liquid, cooled to −50°, is thrown into water, a large volume of chlorine is liberated, and the solution contains arsenious acid and not arsenic acid; it follows that no arsenic pentachloride is formed. If liquid chlorine at −35° is brought in contact with arsenic chloride at the same temperature, and the temperature is allowed to rise slowly, the arsenic chloride melts, and the two liquids gradually mix by diffusion without any development of heat or any other evidence of combination.

Stannic chloride free from excess of chlorine solidifies at −33°, and forms small, white crystals. Like arsenic chloride, it absorbs large quantities of chlorine at a low temperature, with considerable increase in volume, and the freezing point of the solution is much lower than that of the stannic chloride. C. H. B.

Preparation of Boron. By H. C. C. MAISCH (*Chem. Centr.*, 1889, ii, 905; from *Chem. tech. Centralanzeiger*, **7**, 359—360, 369, 379).—The author has prepared boron by reducing anhydrous borax with magnesium powder: 8 grams of magnesium and 15 grams of borax are suitable proportions. J. W. L.

Reduction of Oxygen Compounds by Magnesium. By C. WINKLER (*Ber.*, **23**, 44—57).—The exceptionally high heat of combustion of magnesium has led the author to examine the action of the powdered substance on the oxygen compounds of a large number of metals. In this paper the results are given so far as Mendeléeff's first group is concerned.

In the case of the alkali metals, the carbonates were employed as with the exception of lithium oxide, the oxides of these metals can only be obtained pure with difficulty, but in the other cases the oxides were used. Sufficient magnesium powder was added to combine with the whole of the oxygen present in the carbonate or oxide; the latter being carefully dried by ignition, and intimately mixed in a warmed mortar with the necessary quantity of magnesium powder. After making a preliminary examination with very small quantities, to ascertain the behaviour of the mixture on heating, a somewhat larger quantity was heated in a tube closed at one end, over the flame of an ordinary burner, or, if necessary, by a blowpipe.

Lithium.—The reaction takes place below a red heat, and is extremely violent; with 0·2 gram, an explosion takes place, and the tube

is destroyed. With smaller quantities, the whole becomes red-hot, but the tube remains intact. The product has no metallic appearance, but evolves hydrogen when placed under water, and must therefore contain lithium.

Sodium.—The mixture becomes first black, and when a red heat is reached, a violent reaction takes place, a bright sodium flame issuing from the mouth of the tube, the interior of which becomes coated with a mirror of metallic sodium. Part of the mixture is ejected from the tube, whilst the residue consists of carbon and magnesia. The reaction does not succeed equally well in all cases. If freshly ignited magnesia be added, a mixture of magnesia, charcoal, and sodium is obtained, which decomposes water violently, and ignites the evolved hydrogen.

Potassium.—The reaction in this case proceeds much more quietly, no violent evolution of potassium taking place under any circumstances, and the temperature necessary to commence the reaction appears also to be lower than with sodium. The mixture is preferably heated in a porcelain boat in a current of hydrogen, the potassium condensing as a mirror on the cooler parts of the tube. The residue consists of magnesia and charcoal, and has only a slightly alkaline reaction, showing that the potassium is completely driven off. This method might perhaps be employed as a technical method for the preparation of potassium, but it has the disadvantage that no gas is formed to carry forward the potassium vapour, and the formation of the explosive compound of carbon monoxide and potassium is not avoided. The formation of this compound is due to the fact that two atoms of oxygen are more readily given off than the third, and if 1 mol. of potassium carbonate be heated with 2 atoms of magnesium, this compound and magnesia are the sole products; the author therefore concludes that it has the formula COK_2. If sufficient magnesium is present to combine with all the oxygen, the explosive compound is only formed when the mixture is heated gradually, and to a moderate temperature.

Potassium hydroxide is also readily reduced by magnesium, and in this case the above explosive compound cannot, of course, be formed. When the mixture is heated in a tube closed at one end, a somewhat violent reaction takes place, hydrogen being evolved, and a mirror of metallic potassium formed. If a few grams be heated in a current of hydrogen, the reaction is so violent as to become dangerous, but a mixture of 36 parts of potash, 24 parts of magnesium powder, and 56 parts of magnesia may be heated without any risk, the metal distilling over quietly, and a residue of magnesia remaining behind. The reaction might also be moderated by allowing the fused potash to flow on to heated magnesium bars. Either method would probably enable potassium to be obtained much more cheaply than at present.

Rubidium.—The carbonate of this metal behaves with magnesium in a manner very like that of potassium carbonate. Heated in a tube closed at one end, the reaction commences at a moderate red heat, and a mirror of metallic rubidium is obtained. The latter is also formed when the mixture is heated in a porcelain boat in a current of

hydrogen. The residue, which also contains rubidium, decomposes water with violence, and takes fire in the air. Metallic rubidium is most readily prepared by this method.

Cæsium.—The mixture of cæsium carbonate and magnesium powder blackens on heating from separation of charcoal, but no metallic cæsium is obtained even in the blowpipe flame. Small quantities of potassium and rubidium contained as impurities are volatilised, so that it is thus possible to separate these metals from cæsium. The residue consisted of unaltered magnesium, magnesia, charcoal, and cæsium oxide.

Copper.—Cuprous oxide is acted on by magnesium at a moderate heat, with a hissing noise, the mixture being partially ejected from the tube. The residue consists of a mixture of copper and magnesia. Cupric oxide and maguesium explode violently on heating, the tube being destroyed.

Silver.—Silver carbonate and magnesium unite with a slight explosion, the contents of the tube being ejected, but the tube remains intact. With silver oxide, the reaction is much more violent, and a loud explosion takes plaee.

Gold.—When aurons oxide and magnesium are heated, the former quietly decomposes into gold and oxygen, the magnesium taking no part in the reaction.

From these results it follows that the observation of Warren (this vol., p. 195) that magnesium does not reduce the alkalis and alkaline earths, is incorrect. With the exception of eæsium, all the alkali metals are reduced, the intensity of the reaction decreasing with the increase of atomic weight. In the sub-group the reverse is the case, the apparent exception in the case of gold being due to the instability of its oxide at high temperatures. H. G. C.

Some Properties of Sodium Perchlorate: Supersaturated Solutions. By A. POTILITZIN (*J. Russ. Chem. Soc.*, **21**, 258—274).—This salt was investigated by Serullas and by Penny, who found that it forms deliquescent, rhombic crystals (not rhombohedra, as quoted in *Gmelin-Kraut. Handb.*, ii, **1**, 211). Potilitzin prepares sodium perchlorate from perchloric acid and sodium hydroxide prepared from sodium. After separating the ferric oxide and alumina, the salt is treated with an excess of perchloric acid, in order to destroy the chlorate and chloride, which are always present in traces. At the ordinary temperature, the salt $NaClO_4,H_2O$ crystallises in lanceolate prisms belonging to the rhombic system; it becomes anhydrous at 45—50°, and at or above 54° the anhydrous salt crystallises out from saturated solutions in the form of long, rectangular prisms. Neither kind of crystal is hygroscopic, but the weight of the anhydrous salt increases slightly on exposure to air. The same anhydrous salt separates out from supersaturated solutions at the ordinary temperature. A supersaturated solution contains not only the anhydrous, but also the hydrated salt, as seen from the fact that the solution solidifies on contact with a crystal either of the hydrated salt, or of the anhydrous salt the surface of which has been converted into the hydrated salt by plunging it for a short time into water. The crys-

tals of the anhydrous salt alone do not cause crystallisation, but dissolve in a supersaturated solution.

The author discusses the different views on supersaturated solutions, and shows that the mechanical theory of heat alone (Coppet) does not explain why certain salts form supersaturated solutions whilst others do not. Again, Shtcherbatcheff's view, that the supersaturation of a solution is due to the formation of a lower hydrate having a greater solubility, does not explain the existence of supersaturated solutions of anhydrous salts. The third view, according to which a supersaturated solution is one of the anhydrous salt, is of older date, and has been defended especially by Nicol (Trans., 1887, 389, &c.). The author shows that this hypothesis is not in accordance either with the change of specific gravity which takes place on dissolution and on dilution of solutions; with thermal data connected with the formation of hydrates and the dissolution of hydrated, dehydrated, and anhydrous salts; with the colour phenomena occurring on dilution or change of temperature; or with the change in the coefficients of refraction and other properties of salt solutions. The author shows that the values of the heats of formation of chlorides in solution from R_2O or RO and 2HCl are not identical, as assumed by Nicol, but that the largest value (27,900 cal.) corresponds with calcium chloride, which, according to Rüdorff, exists in solution as $CaCl_2,6H_2O$. Nicol's views do not explain the existence of solutions of anhydrous salts and of such substances as sulphur. The author shows that, in accordance with Mendeléeff's views on solutions in general, the supersaturated solutions of salts undoubtedly contain the salt in the state of several (probably of all possible) hydrates, as well as in the form of the anhydrous salt; the relative quantity of these changing with varying dilution and temperature. Such solutions can be formed only by the substance forming compounds which are either isomeric or of different composition, and differ in their solubility and crystalline form. B. B.

Allotropic Silver. By M. C. Lea (*Amer. J. Sci.* [3], 38, 237—240 and 241).—The three allotropic forms of silver previously described (this vol., p. 210) are merely the most stable forms amongst a very large number. Modifications were also obtained the body colours of which were blue, many different shades of green, red, yellow, and purple. In one case a soluble modification yielding an intense yellowish-brown solution was obtained, but on addition of sodium phosphate this changed to bright scarlet, and afterwards decolorised with separation of a purple precipitate, and the latter became bluish-green when washed on the filter.

Blue allotropic silver is very stable, and may be kept in the moist state for a long time without undergoing any change, but the gold coloured modification always tends to pass into normal grey silver especially in presence of the mother liquor or of water. The change is produced even by friction of the particles of the dried substance with one another. Both modifications evolve oxygen with hydrogen peroxide.

Both the blue and the golden modifications are attacked by sul

stances which have little action on normal silver. Not only solutions of the halogens, and chlorinating or brominating mixtures, but also alkaline sulphides, potassium permanganate and ferrocyanide, and phosphorous acid produce brilliant blue, green, red, or purple colorations when brushed over dry films of the allotropic silver. Auric, stannic and platinic chlorides do not give these colour reactions, and the haloïd salts of the alkalis also give no colours but convert the allotropic silver into normal silver.

Pure preparations of the blue allotropic silver are converted into the yellow modification by the action of light (compare *loc. cit.*), and afterwards, if the exposure is continued, into grey normal silver.

If a small crystal of iodine is placed on a film of allotropic silver, it produces brilliantly coloured interference rings. C. H. B.

Darkened Silver Chloride not an Oxychloride. By M. C. Lea (*Amer. J. Sci.* [3], **38**, 356—361).—Pure silver chloride was fused and poured into refined petroleum, in which it solidified. When exposed to light under the petroleum, the silver chloride immediately blackened, and the author regards this result as proof that darkened silver chloride does not contain oxygen, and therefore is not an oxychloride.

Pure silver reduced by means of cadmium was heated nearly to redness, and whilst very hot was dropped into petroleum. A small quantity of iodine was then added, and as it dissolved in the petroleum it combined with the silver, until after some time no free iodine remained, and the silver had been converted into a black photo-iodide, which from the conditions of its formation could not be an oxy-salt.

Any satisfactory theory must explain the period of so-called induction when silver chloride is exposed to light, and the fact that the decomposition of the silver chloride is incomplete even after prolonged exposure. According to the author, the period of induction corresponds with the formation of an almost colourless photochloride (Abstr., 1888, 1), which is much more sensitive than the normal chloride, and rapidly darkens after it has once been formed. The decomposition of the silver salt is limited by the reconversion of the subchloride or photochloride into normal chloride by the chlorine liberated from the adjacent particles of chloride which are acted upon by light.

C. H. B.

Peculiar Crystalline Alloy of Copper, Tin, and Lead. By A. French (*J. Soc. Chem., Ind.*, **8**, 36—37).—This crystalline alloy was found within a cavity in the bottom of a cupola furnace, which was being put off after having been used for lead-smelting. The crystals form plates, and flat, lengthy, four-sided prisms. They resist atmospheric oxidation, and are not affected by strong sulphuric or hydrochloric acids. Hot nitric acid attacks them, but there are smaller crystals amongst them which resist this action. Analysis gave—

Pb.	Cu.	Sn.	Sb.	Fe.	Si.	S.	Insoluble in HNO_3.	Total.
66·89	11·32	10·22	3·70	0·75	2·09	0·53	4·50	100·00

D. B.

Ternary Alloys. By C. R. A. WRIGHT and C. THOMPSON (*Proc. Roy. Soc.*, 45, 461—481).—If tin, lead, and zinc are melted together and left at rest in a fused condition, no separation takes place if the proportion of tin exceeds a certain amount, but if the quantity of tin is less than this, the alloy separates into two layers, like certain mixtures of alcohol, ether, and water, each layer consisting of a ternary alloy of the above three metals. The authors have examined the nature of this separation, and the composition of the alloys under different conditions. The method of experiment consisted in maintaining the fused mixture at a temperature of 600—700° for some hours, care being taken to avoid convection currents, and analysing the two layers, which were usually quite distinct. In order to obtain separation, the proportion of tin must not exceed $\frac{3}{8}$ths by weight of the whole. The heavier alloy consists of a saturated solution of zinc in lead containing tin, the lighter consists of a saturated solution of lead in zinc containing tin. The two alloys always correspond with two conjugate points on the solubility curves of zinc in lead-tin, and of lead in zinc-tin. The tin does not distribute itself equally in the two alloys, except when present in a particular proportion, which varies with the ratio of zinc to lead. With less tin than this, the lighter alloy takes up the excess of tin; with more, the heavier takes up the excess. Consequently an indefinite number of mixtures may be prepared in which the heavier alloy will always be the same, the lighter alloy varying in composition, whilst in another set the lighter alloy will remain constant, the lower varying. In the absence of tin, lead dissolves zinc forming an alloy containing 1·24 per cent. of zinc, and zinc dissolves lead forming an alloy containing 1·14 per cent. of lead.

H. K. T.

Compounds of Vanadic Pentoxide with Sulphuric Acid. By L. MÜNZING (*Chem. Centr.*, 1889, ii, 908—909).—In a critical essay on the various compounds of vanadic and sulphuric acids, said to have been prepared by several workers, the author considers that the anhydrous compounds which Fritsche and Ditti claim to have prepared are not obtainable, and that their yellow or orange compound is identical with that of Berzelins. Gerland's octohedral compound, $V_2O_5,3SO_3$, is identical with Berzelius's brown compound.

J. W. L.

Mineralogical Chemistry.

Occurrence of Hydrogen Sulphide and Sulphur in the Stassfurt Salt Deposits. By E. PFEIFFER (*Arch. Pharm.* [3], 27 1134—1137).—In a new shaft sunk near Güsten, compact anhydrit was passed through at a depth of 105 to 133 metres; the salt clay wa also regularly and compactly deposited, but at its contact with rock salt it was permeated by strings of crystallised sulphur as thick as th finger. E. Reichardt first explained such an occurrence of sulphu ascribing it to the action of decomposing vegetable matter collecte

on the shores of the ancient sea, which decomposing substances in contact with anhydrite caused the separation of sulphur and the formation of hydrogen sulphide, whilst the lime set free was converted into calcium chloride by the action of magnesium chloride, magnesia being deposited. The free magnesia is detectable in the salt clay, and the calcium chloride in the secondary product tachydrite. The occurrence of sulphur in these deposits affords some confirmation of Reichardt's view of the origin of the gaseous hydrocarbons so frequently found in quantity in the cavities of the carnallite deposits, which he also ascribes to the decomposition of vegetable matter.

J. T.

Native Lead from Pajsberg, Sweden. By A. HAMBERG (*Zeit. Kryst. Min.*, **17**, 253—263).—Native lead, in distinct crystals, has recently been found at the Harstigen mine, near Pajsberg, in Wermland. It occurs only in open cavities, not filled in with calcite. The forms observed on the crystals collected by the author were: O, ∞O∞, ∞O, 2O2, 5O, ∞O4. An analysis of the lead crystals failed to indicate the presence of any other element. The sp. gr. was found to be 11·372. The author is of opinion that the lead has been reduced by arsenious acid, as arsenic compounds, especially arsenates, are of frequent occurrence in the Wermland mines. B. H. B.

Fluorspar, Opal, Amber, and Diamond. By G. F. KUNZ (*Amer. J. Sci.* [3], **38**, 72—74).—The author describes some crystals of fluorspar found in a cave in Archæan limestone at Macomb, St. Lawrence Co., New York. The cave contained at least 15 tons of the mineral, the crystals being simple cubes of a uniform, light, sea-green colour. The author also describes specimens of a very remarkable amber from an unknown locality in Southern Mexico. The colour is a rich golden-yellow, and the mineral exhibits fluorescence similar to that of uranine. A specimen of fire opal was found near John Davis River, Oregon. It is the first opal found in the United States that exhibits colour. In conclusion, the author notes that a small diamond is said to have been found in Russel Co., Kentucky.

B. H. B.

Artificial Copper-bismuth-glance. By R. SCHNEIDER (*J. pr. Chem.* [2], **40**, 564—573; compare Abstr., 1889, 354).—One gram of finely powdered potassium bismuth sulphide, K_2S,Bi_2S_3, prepared by fusing powdered bismuth (1 part) with potassium carbonate (6 parts) and sulphur (6 parts), is put into a flask (50—60 c.c.), which is then filled with a feebly ammoniacal solution of 0·235 gram. of cuprous oxide in hydrochloric acid, and well shaken. After 8 or 10 days the solution becomes colourless, and a nearly black powder settles down; this is a mixture or compound of cuprous sulphide, bismuth sulphide, potassium sulphide, and bismuth trioxide; it is put into a flask which is filled with a mixture of equal quantities of fresh hydrosulphuric acid and dilute hydrochloric acid (1 : 20), and well shaken. The resulting powder is found to have the same composition as copper-bismuth-glance, and when it is fused assumes the light-grey colour and crystalline fracture of the natural mineral. Its specific gravity at 15° is 6·10, that of the natural mineral being

5·137—5·263 according to Weisbach, and 6·23—6·38 according to Frenzel.

Copper-bismuth-glance is also artificially obtained by fusing cuprous sulphide with bismuth sulphide (equal mols.). It is thus evident that the rational formula of this mineral is Cu_2S,Bi_2S_3.

By passing hydrogen sulphide through a mixture of cuprous chloride (3 mols.) with bismuth trichloride (2 mols.), and fusing the precipitate formed, artificial copper-bismuth ore (Wittichenite), $3Cu_2S,Bi_2S_3$, is obtained. A. G. B.

Metallurgical Products from the Mechernich Lead Works. By A. BRAND (*Zeit. Kryst. Min.*, **17**, 264—268).—Some crystals from the Mechernich lead furnaces were examined by the author, and two types are described in detail. The crystals of the first type were flat, triangular, and irregular, and exhibited a perfect metallic lustre and steel-grey colour. They were found to be twinned octahedra of the regular system, and to give on analysis the following results:—

S.	Cu.	Pb.	Fe.	Total.
18·43	49·73	18·47	13·41	100·04

This is evidently an isomorphous mixture of Cu_2S, Fe_2S, and PbS. A mineral crystallising in the regular system with the composition $2PbS + Cu_2S$ (cuproplumbite) is known, as are also regular crystals of artificially prepared copper-glance. This metallurgical product is consequently chiefly of interest on account of its crystallising in the regular system in the presence of so much iron as Fe_2S.

The crystals of the second type appear to be distinct octohedra. Analysis gave the following results:—

Sb.	Pb.	Cu.	Ni.	Co.	Fe.	S.	Total.
32·80	19·32	41·25	4·60	0·48	0·27	0·66	99·38

This the author considers to be an isomorphous mixture of NiSb,PbS and Cu_2S,PbSb, and Cu_6Sb. B. H. B.

Preparation of Crystallised Iron Disulphide (Iron Pyrites). By E. GLATZEL (*Ber.*, **23**, 37—40).—Iron pyrites may be artificially prepared by the action of phosphorus pentasulphide on ferric chloride. For this purpose, a mixture of ferric chloride (50 grams) and phosphorus pentasulphide (25 grams) is carefully heated in a retort as long as thiophosphoryl chloride distils over rapidly, and then strongly heated until the evolution ceases entirely. On cooling, a greyish-white mass is formed under a crust of unaltered ferric chloride and phosphorus pentasulphide, which may readily be detached. The mass is then treated with water, which removes ferrous chloride, and the residual mixture of iron pyrites and lighter impurities sifted and washed to remove the latter. The reaction is represented by the equation—

$$6FeCl_3 + 2P_2S_5 = 3FeCl_2 + 3FeS_2 + 4PSCl_3.$$

The iron pyrites thus obtained forms microscopic, sharply-developed crystals, consisting of pentagonal dodecahedra or cubes, or combinations of these, and also combinations of the pentagonal dodecahedron

and octohedron. The yield is very good, but considerable quantities are lost in the washing process. H. G. C.

Minerals from the Tyrol and other Localities. By H. v. FOULLON (*Jahrb. f. Min.*, 1889, ii, Ref. 414—420; from *Jahrb. k.k. geol. Reichsanst.*, **38**, 1—33).—This memoir is divided into nine heads. The first deals with the minerals found at Hall, in the Tyrol, the minerals described being galena, brennerite, and bloedite. Of the last two, a number of analyses are given. The second section is devoted to a description of the brucite which occurs with carbonates of calcium, magnesium, and strontium at the Steinpass, near Imst, in the Tyrol. The specimen examined so closely resembled gurhofian, that the author was induced to examine that mineral from Gurhof, Windhof, and Altenberg. The results of the analysis of the specimen from Windhof showed it to be composed of 4·80 per cent. of serpentine, 89·00 per cent. of calcium and strontium carbonate, 3·89 per cent. of magnesium carbonate, and 1·48 per cent. of magnesium hydrate. A product of the alteration of serpentine so rich in lime is remarkable, and it would be of interest to know whether other serpentines when altered actually yield magnesium hydrate.

The remaining sections deal with (3) realgar from Wolfsberg, in Carinthia; (4) minerals from Truskawiec, in Galicia; (5) minerals from Közép-hegy, near Rosenau, in Upper Hungary; (6) quartz from Bereghszász, (7) siderite in the opal of Nagy Laáz, in Hungary; (8) similarity of the Japanese and Greek glaucophane rocks; and (9) similarity of the eruptive rocks of the province of Karassi, in Asia Minor, and those of Schemnitz, in Hungary. B. H. B.

Plattnerite from Idaho. By H. A. WHEELER (*Amer. J. Sci.* [3], **38**, 79).—The author notes a new occurrence of plattnerite (lead dioxide) from one of the lead mines of the Cœur d'Alêne district, Idaho. The specimen was irregular, massive, and of an iron-black colour, with a chestnut-brown streak. The hardness is 5 to 5·5, and the sp. gr. 9·411. Analysis gave the following results:—

PbO_2.	SiO_2.	Fe_2O_3.	Total.
96·63	1·62	1·12	99·37

The percentage of lead is 83·69. This rare mineral is called a doubtful species in Dana's System of Mineralogy (compare next abstract). B. H. B.

Plattnerite from Idaho. By J. D. HAWKINS and E. N. HAWKINS (*Amer. J. Sci.* [3], **38**, 165—166).—Two analyses of plattnerite from a mine near Wallace, Shoshone Co., Idaho. The results were as follows:—

PbO_2.	ZnO.	SiO_2.	Al_2O_3.	Fe_2O_3.	Total.
90·99	0·07	2·68	0·28	5·69	99·71
91·03	0·07	3·00		5·86	99·96

The sp. gr. of the powdered mineral is 7·25, which seems to be more in accordance with the sp. gr. of massicot (8·0) than with that given by Wheeler (preceding abstract). The specimen was found in a fissure vein in quartzite, and appears to be a direct alteration from galena. B. H. B.

Urao (Natural Soda). By T. M. Chatard. (*Amer. J. Sci.* [3], **38**, 59—64).—The salts described by the author were obtained by the spontaneous solar evaporation of the water of Owen's Lake, California, and consequently are regarded as minerals. The urao of Venezuela, analysed by Boussingault, is an almost theoretically pure salt, showing only a small loss of water and a trifling increase of sodium hydrogen carbonate. The existence of a native sodium sesquicarbonate, $Na_2CO_3,2NaHCO_3 + 3H_2O$, to which the name of trona has been given, rests on an analysis by Klaproth, and to this mineral the numerous published analyses of natural sodas have been referred. A recalculation of these analyses shows that none of them agree with this formula, but that the salts were uraos, with a widely varying excess of one or the other of the two carbonates. Additional proof was afforded by the fact that the artifical salt produced by Winkler's method was a urao with an excess of sodium hydrogen carbonate. Thus, there is no such salt, either natural or artificial, as sodium sesquicarbonate, but the true salt has the formula $Na_2CO_3,NaHCO_3 + 2H_2O$, although the presence of an excess of sodium hydrogen carbonate may occasionally give results approaching the composition of a sesquicarbonate. The five salts of which analyses are appended were obtained from Owen's Lake. Nos. 1 and 2 are from the same specimen, and were formed in an artificial ground vat, No. 1 being well crystallised and translucent, sp. gr. 2·1473, and No. 2 the undissolved portion of the first product. No. 3 was formed on a branching grass-root. No. 4 is from a small lagune on the east side of the lake. No. 5 was formed in a vat which was dug in the beach, and allowed to fill with permeating water from the surrounding soil.

	1.	2.	3.	4.	5.
Insol. inorganic.	0·02	0·22	2·92	0·40	4·10
Insol. organic ..	—	—	0·14	0·12	0·27
SiO_2	—	0·10	0·05	0·09	0·04
CaO	—	—	—	0·06	—
MgO..........	—	—	—	0·02	—
K_2O	—	—	—	trace	—
Na_2O..........	40·99	41·26	40·22	40·08	39·36
Cl............	0·19	1·57	2·73	0·21	1·83
SO_3	0·70	0·79	0·76	0·63	0·84
CO_2	38·13	37·00	35·24	37·50	35·10
H_2O	20·07	19·62	18·31	19·94	18·58
Total	100·10	100·56	100·37	99·05	100·12
O = Cl	0·04	0·35	0·61	0·05	0·41
	100·06	100·21	99·76	99·00	99·71

Each of these samples is urao, differing very slightly from the theoretical figures—

Na_2CO_3.	$NaHCO_3$.	H_2O.
46·96	37·17	15·93

A series of experiments was undertaken in order to determine the conditions under which urao is formed. In no case, no matter what the relative proportions of the salts might be, was any other mixed carbonate but urao obtained. It is therefore remarkable that this salt, which seems to be the natural form of sodium carbonate, should either not be mentioned in treatises on the sodium salts, or be confounded with another which does not appear to exist at all.

B. H. B.

Kaliborite, a new Boron Mineral. By W. Feit (*Chem. Zeit.*, **13**, 1188).—In the mines at Schmidtmannshall, near Aschersleben, not only are boracite, pinnoite, and stassfurtite found in the upper layers of the kainite, but there is also another mineral present, in fragment, either quite pure or associated with the above minerals. Disregarding the 1 to 2 per cent. of sodium chloride it contains, it has the following composition:—

K_2O.	MgO.	B_2O_3.	H_2O.
6·48	12·06	57·46	24·00 = 100

from which is deduced the complex formula—

$$K_4Mg_9B_{48}O_{83} + 39H_2O, \text{ or } 2K_2B_6O_{10} + 9MgB_4O_7 + 39H_2O.$$

This new mineral is called *kaliborite;* its sp. gr. is 2·05, and superficially it resembles pinnoite, but its fracture resembles that of kieserite, and, like the latter mineral, it falls to powder under water; this is attributed to the solution of the small proportion of sodium chloride which probably acts as a cement The powder consists of microscopic, colourless, sharp-edged granules, clear as water, but on which crystalline faces cannot be detected. The mineral is slightly soluble in water yielding an alkaline solution, but is not decomposed by it; it dissolves readily when warmed with mineral acids. Before the blow-pipe, it fuses with difficulty to a colourless glass.

It is suggested that kaliborite is formed from pinnoite, the strong potash solutions in the mine abstracting magnesium and introducing potassium, for although laboratory experiments have failed to produce kaliborite by soaking pulverised pinnoite in saturated solutions of potassium chloride, yet under the conditions in the earth it may be probable, and a fragment was found consisting of pinnoite grown on boracite, a portion of the former being covered over with a layer of the new mineral, 2 to 10 mm. thick.

D. A. L.

Descloizite from new Localities. By W. F. Hillebrand (*Amer. J. Sci.* [3], **37**, 434—439).—The author gives the three following analyses of descloizites from new localities in America:—

	PbO.	CuO.	FeO.	ZnO.	V_2O_5.	As_2O_5.	P_2O_5.	H_2O.	Cl.
I.	55·93	1·15	0·70	15·94	20·80	0·32	0·27	4·37	—
II.	56·01	1·05	0·07	17·73	20·44	0·94	0·26	2·45	0·04
III.	57·00	11·21	trace	4·19	19·79	1·10	0·19	2·50	0·07

	SiO_2.	CaO.	MgO.	K_2O.	Na_2O.	CO_2.	Total.
I.	0·18	0·10	0·06	—	—	—	99·82
II.	1·01	0·04	0·03	—	—	—	100·07
III.	0·80	1·01	0·04	0·10	0·17	0·82	98·99

No. I is a friable, uncrystallised material, from Mayflower Mine, Beaverhead Co., Montana. It has a dull-yellow to pale-orange colour, and consists chiefly of a vanadate. The percentage of water is double that required by descloizite, $R_2(OH)VO_4$; but this is not considered sufficient cause for separating the mineral from descloizite, although the close agreement of water-determinations made on different samples appears to indicate the correctness of the formula

$$2[R_2(OH)VO_4] + H_2O.$$

No. II, from the Commercial Mine, Georgetown, New Mexico, is one of the most interesting occurrences of descloizite known, because of the extreme brilliancy of colouring of the mineral. It varies from yellow through all shades of orange-red to deep reddish-brown.

No. III was found in the Lucky Cuss Mine, Tombstone, Arizona, as an incrustation on quartz. Its colour is brown, its hardness 3·5, and its sp. gr. 5·88. The low total in the analysis is probably owing to a loss of zinc. There can be no doubt that the general formula for this vanadate is that of descloizite. It closely resembles the descloizite of Penfield (Abstr., 1884, 24), the cupro-descloizite of Rammelsberg (Abstr., 1885, 731), and perhaps the tritochorite of Frenzel (Abstr., 1882, 473). The specific identity of all these substances seems highly probable, and it might be well to designate them by some distinctive name. For this purpose *cupro-descloizite* is the most suitable.
B. H. B.

Pharmacolite from the Vosges. By E. JANNETAZ (*Jahrb. f. Min.*, 1889, ii, Ref. 409; from *Bull. Soc. fran. min.*, **11**, 212—215).—The crystals found at Sainte-Marie-aux-mines, Vosges, are, as usual, grouped radially. They have a sp. gr. of 2·535, and, after subtraction of 0·70 per cent. of silica and 0·35 per cent. of ferric oxide, gave on analysis the following results:—

As_2O_5.	P_2O_5.	CaO.	MgO.	H_2O.	Total.
51·05	0·30	24·54	0·50	24·00	100·39

B. H. B.

Silicic Acids. By G. F. BECKER (*Amer. J. Sci.* [3], **38**, 154—157).—The silicic acids usually assumed to be necessary to account for the natural silicates are orthosilicic acid, H_4SiO_4, metasilicic acid, H_2SiO_3, polysilicic acid, $H_4Si_3O_8$, and disilicic acid, $H_2Si_2O_5$. Groth, however, has shown that polysilicic acid may be regarded as a combination of $H_2Si_2O_5$ and H_2SiO_3, thus reducing the number of acids to three. If disilicic acid is, as Groth suggests, a constituent of the

alkaline felspars, it is remarkable that it is not of more frequent occurrence independently, for whilst polysilicates are amongst the most abundant minerals found, disilicates are represented only by petalite and milarite. The author proposes to simplify the series of acids in another way, namely, by regarding H_2SiO_4 and $H_4Si_3O_8$ as forming $4H_2SiO_3$, an hypothesis which is supported by the fact that both of the constituents are very abundant in nature. There are, too, grounds in the behaviour of the silicates favourable to this view of their constitution. It remains to be considered how disilicic acid is to be regarded. This the author regards as a polysilicic acid from which orthosilicic acid has been removed, a process represented by $3H_4Si_3O_8 - H_4SiO_4 = 4H_2Si_2O_5$. The constitution of petalite and milarite appears to be insufficiently established, and it is not necessary to assume for them an acid not known to exist elsewhere.

B. H. B.

New occurrence of Gyrolite. By F. W. Clarke (*Amer. J. Sci.* [3], **38**, 128—129).—A mineral, lining crevice veins in the New Almaden quicksilver mine in California, locally supposed to be white fluorspar, is found by the author to be gyrolite, having the following composition :—

H_2O.	SiO_2.	$Al_2O_3 + Fe_2O_3$.	CaO.	K_2O.	Na_2O.	F.
14·60	52·54	0·71	29·97	1·56	0·27	0·65

The gyrolite is obviously not perfectly pure, but it agrees approximately with the formula $Ca_2Si_3O + 3H_2O$. B. H. B.

Artificial Magnesia Mica. By K. v. Chroustschoff (*Zeit. Kryst. Min.*, **17**, 303; from *Tschermak's min. Mitth.*, **9**, 55).—An artificially prepared glass, having approximately the composition of a basalt free from felspar and poor in iron, was pulverised and melted in a platinum crucible with the constituents of an iron-magnesia mica, amorphous silicic acid, and a mixture of potassium silicofluoride, sodium fluoride, and aluminum fluoride. The product of the melting consisted of brown tablets of mica, spinel, and glass. The mica (I) and spinel (II) gave on analysis the following results :—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	K_2O.	Na_2O.	F.	Total.
I.	39·11	18·09	2·17	8·55	trace	21·02	7·23	1·74	1·65	99·56
II.	—	63·15	4·19	10·82	—	22·85	—	—	—	101·01

B. H. B.

Barytic Felspars from Sweden. By L. J. Igelström (*Jahrb. f. Min.*, 1889, ii, Ref. 409—410; from *Bull Soc. fran. Min.*, **11**, 263—264).—At the Sjö Mine, Örebrö, a red felspar, resembling the hyalophane of Jacobsberg, occurs in association with garnet, specular iron ore, hausmannite, rhodonite. On analysis, the results given under I were obtained :—

	SiO_2.	Al_2O_3.	FeO + MnO.	BaO.	MgO.	CaO.	$K_2O + Na_2O$.	Total.
I.	61·90	15·80	5·00	9·58	1·30	0·40	6·02	100·00
II.	54·15	29·60	—	1·26	1·52	1·00	12·47	100·00

The second analysis, II, is that of a white felspar, optically resembling albite, but much more basic. It occurs in association with rhodonite and calcite.

B. H. B.

Andesine from Bodenmais. By M. SCHUSTER and H. v. FOULLON (*Zeit. Kryst. Min.*, **17**, 300; from *Jahrb. k.k. Geol. Reichsanst.*, **37**, 219).—Analysis of this felspar gave the following results:—

SiO_2.	Al_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	Fe_2O_3.	S.	Total.
59·22	25·88	7·08	0·28	0·54	6·79	0·96	0·03	100·78

This composition is that of the mixture of albite and anorthite represented by the formula Ab_7An_4. The optical properties of the felspar are intermediate between those of the mixtures Ab_2An_1 and Ab_3An_2. The angle, for instance, made by the direction of extinction with the edge formed by the faces 0P and $\infty\breve{P}\infty$ on a cleavage plate taken parallel to 0P is $-1° 47'$, the corresponding angles in the mixtures Ab_2An_1 and Ab_3An_2 being $-0° 35'$ and $-2° 12'$ respectively.

B. H. B.

Cossaïte from the Upper Susa Valley. By G. PIOLTI (*Jahrb. f. Min.*, 1889, ii, Ref. 428; from *Atti Acc. Sci. Turin*, **23**, 7).—This mineral occurs interbedded in lime mica schists. It is of an apple-green colour, and easily yields a white powder. It looks as if it were amorphous, but under the microscope is seen to be composed of a number of small plates. Thin sections polarise very distinctly, and the mineral is seen to be anisotropic and biaxial. Its hardness is 2 5, and its sp. gr. 3·07. Analysis gave the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	Li_2O.	Na_2O.	K_2O.	H_2O.	Total.
46·49	40·68	2·68	trace	4·75	1·33	4·57	100·50

According to Dana, cossaïte is identical with paragonite. The author, however, regards this mineral as cossaïte, and is of opinion that cossaïte should not be classed as onkosin, but as a member of the mica group.

B. H. B.

Epidote and Muscovite. By H. v. FOULLON and V. GOLDSCHMIDT (*Zeit. Kryst. Min.*, **17**, 299—300; from *Jahrb. k.k. geol. Reichsanst.*, **37**, 1).—Analysis I gives the composition of epidote from a coarse-grained glaucophane schist from the island of Syphnos; Analysis II that of pale-green muscovite from the glaucophane schist of Syra:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Ignition.	Na_2O.	H_2O.	Total.
I.	40·23	23·74	11·95	0·50	20·49	0·72	2·35	—	—	99·98
II.	49·34	23·69	6·84	—	1·25	2·97	4·40	0·78	10·74	100·01

B. H. B.

Aegirine. By J. MACHADO (*Zeit. Kryst. Min.*, **17**, 304, from *Tschermak's min. Mitth.*, **9**, 318).—The augite from the coarse-grained nepheline syenite of Barriero, Minas Geraës, Brazil, proved to be aegirine, having the following composition:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	Ignition.	Total.
51·60	1·92	26·29	4·20	4·25	1·15	1·05	8·89	0·56	99·91

This represents a mixture of $3NaFeSi_2O_6$, $1Na_2Al_2SiO_6$, $2CaFeSi_2O_6$, and $2CaMgSi_2O_6$. B. H. B.

Inesite, a Manganese Silicate from Dillenburg. By A. Schneider (*Zeit. Kryst. Min.*, **17**, 298—299; from *Jahrb. preuss. geol. Reichsanst*, 1888, 472).—At Nanzenbach, near Dillenburg, manganese ore is mined in a contaet-vein between clay-slate and diabase, the ore being chiefly manganese silicate in amber-yellow masses. This silicate is a mixture similar to klipsteinite. Besides this ore and manganite, psilomelane, wad, pyrites, native copper, and anthracite occur. At the sides of the vein, a new mineral, *inesite* (from ἶνες, muscles), has been found in radiated masses of a reddish colour. It has a hardness of 6, and gave on analysis—

SiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	Total.
43·92	0·29	0·69	37·87	8·40	0·33	9·22	100·72

Taking into account the fact that the mineral is slightly altered, the most probable formula appears to be $(MnCa)(MnOH)_2Si_3O_8 + H_2O$. The crystals are asymmetrical, the axial ratio being $a : b : c = 0·9753 : 1 : 1·3208$: $\alpha = 92° 18'$, $\beta = 132° 56'$, $\gamma = 93° 51'$. The mineral most closely resembling it is the hydro-rhodonite of Engström, but this, although containing the same amount of silica, contains less manganese oxide and more magnesia. B. H. B.

Peridotite from Arkansas. By J. C. Branner and R. N. Brackett (*Amer. J. Sci.* [3], **38**, 50—59).—This rock, which extends over an area of 2400 feet by 1600 feet, occurs in association with palæozoic and cretaceous rocks, and is shown by the coloured geological map accompanying the memoir to be of eruptive origin. The eruption took place at the close of the cretaceous period. The specific gravity of a comparatively unaltered variety was found to be 2·728 to 2·651, whilst that of a highly decomposed variety was 2·317. The latter is traversed by veins of barytes and serpentine. The rock is rendered porphyritic by crystals of olivine and brownish-yellow mica. The olivine is almost always altered into serpentine, and then frequently exhibits trichites of magnetite. The ground-mass consists of augite, perovskite, and magnetite. Enstatite and titaniferons iron are absent, and garnet is of rare occurrence. The rock contains 0·89 per cent. of titanic anhydride. B. H. B.

Porphyrite Bosses in New Jersey. By J. F. Kemp (*Amer. J. Sci.* [3], **38**, 130—134).—The author describes, with the aid of a map, the eruptive rocks in the north-western portion of New Jersey. There are eight exposures in all. The rocks are to be classed with the porphyrites according to the types systematised by Rosenbusch, and might be termed biotite-augite-porphyrite. They agree with the porphyrites of Thuringia in composition, structure, and alteration-products. The author gives the following analyses of the rock from two localities (1 and 2) and of the biotite (3):—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	P_2O_5.	Ignition.	Total.
1.	40·47	11·86	17·44	16·80	3·10	4·21	1·90	—	3·60	99·38
2.	31·80	18·78	15·20	14·60	3·32	5·07	1·10	0·95	8·10	98·92
3.	34·61	15·74	8·52	trace	20·03	17·14	trace	—	2·80	98·84

The sp. gr. of No. 1 is 3·102, that of No. 2 is 2·939. The former effervesced, the latter did not. Alteration consequently lowers the specific gravity. B. H. B.

New Meteorite from Mexico. By J. E. WHITFIELD (*Amer. J. Sci.* [3], **37**, 439—440).—The author describes a mass of meteoric iron weighing 33 kilos., found on La Bella Roca, a peak of the Sierra de San Francisco, in the State of Durango. The date of its discovery and the name of the finder are unknown. The composition of the metallic portion is as follows :—

Fe.	Ni.	Co.	P.	S.	C.	Total.
91·48	7·92	0·22	0·21	0·21	0·06	100·10

On one side of the meteorite there are large, deep pittings, greater in diameter just below than immediately at the surface. Remains of a substance that evidently originally filled the cavities proved to be troilite having the composition—

NiS.	FeS.	Fe.
2·13	85·27	9·37

The exposed portions of the troilite were greatly decomposed, and gave on analysis—

NiS.	FeS.	Fe_2O_3.	H_2O.
2·07	37·51	37·8	19·85

The deep pittings were probably formed by the removal of troilite nodules while the mass was hot, and by the subsequent weathering. Nodules of troilite occur throughout the mass, but the pittings have been formed only on the front side of the meteorite. Thin sections of the meteorite, when etched, show Widmannstättian figures and dark diagonal bands of troilite. B. H. B.

Meteorite from Migheï, Russia. By S. MEUNIER (*Compt. rend.*, **109**, 976—978).—This meteorite fell on June 9th, 1889, at Migheï, in the south of Russia. It is a dark, greenish-black, friable, earthy substance which soils the fingers and paper; sp. gr. at 12° = 2·495. In thin sections under the microscope it is almost entirely opaque, with small crystalline nuclei consisting chiefly of magnesian pyroxene with some peridote. It contains 0·867 per cent. of a very fine magnetic substance consisting almost entirely of iron with a little nickel, and there are also a few grains of pyrrhotine; 85·167 per cent. of the meteorite is soluble in acids, and has sensibly the composition of peridote, SiO_2, 36·21 ; MgO, 34·91 ; FeO, 26·48 = 97·60. The inorganic part of the insoluble portion has the composition—

SiO_2.	MgO.	FeO.	CaO.	Al_2O_3.	Mn and Cr oxides.	
58·42	28·04	10·99	3·04	1·12	traces	= 101·61

The meteorite contains 4·72 per cent. of organic matter which, when heated to redness in a current of hydrogen, splits up into carbon and a small quantity of a bituminous substance with a powerful odour. If the meteorite is heated with alcohol, it yields 0·056 per cent. of a yellow resin very similar to the kabaite of Wöhler.

When the meteorite is treated with water, it yields a colourless, limpid solution which has an odour of amber, and contains a small quantity of organic matter, but it also contains some inorganic substance, amounting to 1·728 per cent. of the meteorite, which with barium chloride, gives a heavy, white precipitate, and with silver nitrate a brilliant red, curdy precipitate insoluble in nitric acid. In contact with the mother liquor, it is partially converted into colourless, hyaline, highly refractive crystals; when exposed to light, it rapidly blackens. The exact nature of this substance has still to be determined. C. H. B.

New Meteorite from Chili. By F. v. SANDBERGER (*Jahrb. f. Min.*, 1889, ii, Mem., 173–180).—The author describes a meteorite found at Carcote, in Chili. It was originally mistaken for silver ore. The main portion of the mass is of a light-grey to whitish colour, and is as hard as quartz. The specific gravity of the mass, after removal of nickel-iron, was found to be 3·466. In addition to minute grains of chrome-iron ore, the meteorite contains grains of two distinct silicates. A portion, 0·476 per cent., of the meteorite was soluble in distilled water, and gave on analysis—

CaO.	MgO.	SO_3.	KCl, &c.
33·83	8·40	27·52	30·25

Hydrochloric acid dissolved the silicate which formed 38·88 per cent. of the mass. This consisted of colourless grains which behaved like olivine under the microscope, and which gave on analysis—

SiO_2.	MgO.	FeO.	Al_2O_3.
38·35	35·83	25·28	0·54

This is the composition of an olivine fairly rich in iron. The second silicate formed 40·73 per cent. of the meteorite. It gave on analysis—

SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.
57·43	5·20	10·07	20·36	2·85	3·35	0·74

This is obviously an alkali-bearing compound of the diopside group, a mineral which has hitherto but rarely been met with. Black grains of chrome-iron ore disseminated throughout the meteorite form but 1·39 per cent. of the mass. The troilite, which forms 5·83 per cent. of the mass, is not distinguishable from ordinary magnetic pyrites. The nickel-iron gave on analysis—

Fe.	Ni + Co.	Mn.	Cu + Sn.	P.
87·08	8.85	1·44	0·60	2·03

This is similar to the composition of the nickel-iron from the meteorite of Deesa. As the alteration-products contain the same elements in equal proportions, the ferric oxide, nickel oxide, and manganese oxide may be calculated as metal. This gives 8·36 per cent. of the mass, which with 1·66 per cent. of unaltered nickel-iron, represents 10·02 per cent. of the meteorite. Minute quantities of the rhabdite of G. Rose also appear to be present. The most remarkable substance, however, occurring in this meteorite is dull-black, has great hardness (9), is not attacked by acids, and consists exclusively of carbon. In one place it forms a segregation 3 mm. in breadth, and appears to be black diamond. Other carbonaceous matter is present, but has not been accurately estimated. The results of the investigation are of considerable interest, as this meteorite represents a new type for Chili—a country in which numerous meteorites have been found. Similar meteorites are, however, known in other districts. Thus, this meteorite resembles the Altianello meteorite which fell on February 15, 1883, and probably also that of New Concord, Ohio.

B. H. B.

Organic Chemistry.

Arrangement in Space of the Atoms in the Molecule of Carbon Compounds containing Nitrogen. By A. HANTZSCH and A. WERNER (*Ber.*, **23**, 11—30).—At the present time a certain number of geometrically isomeric compounds are known in which the isomerism cannot be explained in the same manner as in the case of fumaric and maleïc acids (Abstr., 1888, 35). The compounds in question are the isomeric mono- and di-oximes of benzil, the two benzaldoximes, the two ethyl hydrogen oximidosuccinates, the modifications of the hydroxamic acids, and lastly the two isomeric parazoxytoluenes, and trinitroazotoluenes.

In order to explain the existence of isomeric benzil mono- and di-oximes, Auwers and V. Meyer assume that Van't Hoff's second hypothesis (according to which isomeric compounds of the general formula $\begin{matrix}R_1\\R_1\\R_2\end{matrix}\!\!>C—C\!<\!\!\begin{matrix}R_1\\R_1\\R_2\end{matrix}$ cannot exist) does not hold true in all cases, but that under certain conditions, three geometrically isomeric compounds of such a formula may be obtained (these Abstr., 1888, 549, 597). The existence of two isomeric benzaldoximes has been explained by Beckmann (Abstr., 1889, 608) on the assumption of a different structure of the oximido-group in the two compounds, but Goldschmidt considers this explanation to be incorrect (this vol., p. 253).

An examination of the above compounds shows that all of them contain one or more nitrogen-atoms. The authors point out that up to the present time geometrical considerations concerning the

arrangement of the atoms in the molecule have been for the most part confined to the carbon-atom, and it therefore appeared to them that an application of the same principles to the nitrogen-atom might lead to an explanation of the above cases of isomerism, without making any modification of Van't Hoff's second hypothesis.

The following consideration forms the starting-point of the theory proposed. If Van't Hoff's first hypothesis, that "the valencies of the carbon-atom are equally distributed in space, and correspond to the corners of a regular tetrahedron inscribed in a sphere," be accepted, it is manifest that in the cyanogen compounds, and in those rings of carbon- and nitrogen-atoms in which all three valencies of the latter are combined with carbon, these valencies cannot lie in the same plane as the nitrogen-atom. This is expressed generally as follows:—

The valencies of the *triad* nitrogen-atom do not *necessarily* lie in the same plane as the nitrogen-atom itself.

From this consideration is deduced the hypothesis that "in certain compounds the valencies of the nitrogen-atom are directed towards the corners of an irregular tetrahedron, the nitrogen-atom itself occupying the fourth corner."

On this hypothesis the nitrogen-atom may be in a certain sense represented as a tetrahedron, and, therefore, when a nitrogen-atom is united by two of its valencies either to a carbon-atom or to a second nitrogen-atom, we may have cases of isomerism similar to that of fumaric and maleïc acids. Thus a compound of the formula $XY:C{=}N\cdot Z$ should exist in two forms, $\begin{array}{l} X\cdot C\cdot Y \\ \;\;\;\| \\ \;\;\;N\cdot Z \end{array}$ and $\begin{array}{r} X\cdot C\cdot Y \\ \| \;\;\;\; \\ Z\cdot N \;\;\;\; \end{array}$, the compound $X\cdot N{=}N\cdot Y$ in two forms, $\begin{array}{l} N\cdot X \\ \| \\ N\cdot Y \end{array}$ and $\begin{array}{r} N\cdot X \\ \| \;\;\;\; \\ Y\cdot N \end{array}$.

It would further follow from this hypothesis that compounds of the formula $N \begin{array}{l} \diagup R_1 \\ - R_1 \\ \diagdown R_2 \end{array}$ might possibly exist in optically isomeric forms, and that isomeric hydrazines of the formulæ $\begin{array}{c} X\cdot N\cdot Y \\ | \\ U\cdot N\cdot Z \end{array}$ and $\begin{array}{c} X\cdot N\cdot Y \\ | \\ Z\cdot N\cdot U \end{array}$ might also be obtained. Such compounds are not, however, at present known.

According to this theory, the above-mentioned special cases of isomerism receive the following explanation:—

Benzaldoxime can exist in the two following forms, $\begin{array}{l} H\cdot C\cdot Ph \\ \;\;\;\| \\ \;\;\;N\cdot OH \end{array}$ and $\begin{array}{r} H\cdot C\cdot Ph \\ \| \;\;\;\;\;\; \\ HO\cdot N \;\;\;\;\;\; \end{array}$; sufficient data are, however, not available to show which formula corresponds with benzaldoxime, which with isobenzaldoxime.

Benzilmonoxime can exist also in two forms, $\begin{array}{l} Ph\cdot C \text{—} C\cdot Ph \\ \;\;\;\;\;\;\| \;\;\;\;\; \| \\ \;\;\;\;\;\;O \;\;\;\; N\cdot OH \end{array}$ and $\begin{array}{l} Ph\cdot C \text{——} C\cdot Ph \\ \;\;\;\;\;\;\| \;\;\;\;\;\;\;\;\; \| \\ \;\;\;\;\;\;O \;\; HO\cdot N \end{array}$. *Benzildioxime* should exist in three forms:

$$\begin{array}{c}Ph{\cdot}C\text{---}C{\cdot}Ph\\ \Vert\quad\ \ \Vert\\ N{\cdot}OH\ N{\cdot}OH\end{array},\quad \begin{array}{c}Ph{\cdot}C\text{---}C{\cdot}Ph\\ \Vert\quad\ \ \Vert\\ HO{\cdot}N\ \ N{\cdot}OH\end{array},\ \text{and}\ \begin{array}{c}Ph{\cdot}C\text{------}C{\cdot}Ph\\ \Vert\qquad\ \ \Vert\\ N{\cdot}OH\ HO{\cdot}N\end{array}.$$

This agrees well with the facts, two benzilmonoximes and three dioximes being known. The third formula probably represents the γ-dioxime, as that componud yields an anhydride so readily; the β-dioxime, which is the most stable, has probably the second formula, whilst the α-dioxime, which in its properties is intermediate between the other two, has probably the first formula. If these assumptions are correct, the first formula given above for the benzilmonoximes must represent the α-monoxime, and the second the γ-monoxime.

Ethyl Hydrogen Oximidosuccinates.—The two isomeric compounds will be represented by the formulæ $\begin{array}{l}COOEt{\cdot}C{\cdot}CH_2{\cdot}COOH\\ \qquad\ \ \Vert\\ \qquad\ N{\cdot}OH\end{array}$ and $\begin{array}{l}COOEt{\cdot}C{\cdot}CH_2{\cdot}COOH\\ \qquad\ \ \Vert\\ \qquad HO{\cdot}N\end{array}$.

Lossen's substituted hydroxamic acids may also be regarded as geometrical isomerides, having the general formulæ $\begin{array}{l}C_xH_y{\cdot}C{\cdot}OH\\ \qquad\ \ \Vert\\ \quad\ HO{\cdot}N\end{array}$ and $\begin{array}{l}C_xH_y{\cdot}C{\cdot}OH\\ \qquad\ \ \Vert\\ \qquad N{\cdot}OH\end{array}$, but matters are here more complicated, as these tautomeric compounds may exist in desmotropic modifications.

Trinitroazotoluenes.—These two compounds receive the formulæ $\begin{array}{l}N{\cdot}C_6H_3Me{\cdot}NO_2\\ \Vert\\ N{\cdot}C_6H_2Me(NO_2)_2\end{array}$ and $\begin{array}{r}N{\cdot}C_6H_3Me{\cdot}NO_2\\ \Vert\qquad\qquad\\ C_6H_2Me(NO_2)_2{\cdot}N\qquad\qquad\end{array}$.

The Parazoxytoluenes are represented in a similar manner as follows: $O{<}\begin{array}{l}N{\cdot}C_7H_7\\ |\\ N{\cdot}C_7H_7\end{array}$ and $\begin{array}{r}O{<}\begin{array}{l}N{\cdot}C_7H_7\\ |\\ N\end{array}\\ C_7H_7\text{---}\qquad\end{array}$.

To this theory the objection may be possibly raised, that if these considerations were correct the number of such isomerides would be extremely large, whereas, in reality, only a very limited number are known. In answer to this the authors point out that only a very small number of the theoretically possible geometrical isomerides of carbon compounds have been as yet obtained; and that, further, such geometrical isomerides as are here described can, according to the theory, only be formed when the three valencies of the nitrogen-atom are not in the same plane as the atom itself, and it is quite possible that in a large number of instances this condition may not be fulfilled, in which case the number of isomerides corresponding with those discussed above would be greatly diminished. Experiments are now being made to see whether, under any circumstances, optical isomerides of ammonia or hydrazine derivatives can exist.

H. G. C.

Sulphur Compounds in Raw Petroleum and in Petroleum Residues. By C. F. MABERY and A. W. SMITH (*Ber.*, **22**, 3303—3305).—Ohio petroleum contains considerable quantities of sulphur compounds which are present in the largest proportion in the portions boiling between 200 and 300°. The sulphur compounds can be extracted by treatment with concentrated sulphuric acid and, on neu-

tralising the diluted acid solution with lead carbonate (or lime) and evaporating, a salt separates from the solution. When this salt is distilled with steam, the sulphur compounds collect in the receiver in the form of a light yellow oil; this product, which contains 14·97 per cent. of sulphur, was distilled under a pressure of 100 mm. and the following fractions collected:—

Fraction..	80—90°	100—105°	135—140°	150—155°	185—190°
Sulphur..	none	18·23	15·52	16·44	14·21

The fractions boiling above 100° all contained sulphides, but thiophen compounds and mercaptans were absent in every case; those of lower boiling point gave crystalline precipitates with an alcoholic solution of mercuric chloride, whilst the higher fractions gave oily compounds which subsequently solidified when kept or recrystallised from benzene. They all combine with bromine with explosive violence. The fraction boiling at 80—90° combined with bromine, yielding a heavy oil which seems to have the composition $C_{17}H_{14}Br_2$. All the fractions boiling below 135° combined with hydrobromic acid yielding oily products.

Analyses of the mercury compounds showed that the sulphur compounds present are ethyl, propyl, and butyl sulphides.

F. S. K.

Derivatives of Diallyl. By G. Ciamician (*Ber.* **22**, 3326).—A reply to Wagner's note (this vol., p. 223).

Cyanogen Monosulphydrate. By R. Anschütz (*Annalen*, **254**, 262—264).—Pure cyanogen monosulphydrate (flaveanwasserstoff) $C_2H_2N_2S$, can be obtained by passing hydrogen sulphide and excess of cyanogen into alcohol and recrystallising the dark-coloured product from boiling chloroform. It forms pale yellow needles, begins to darken at about 80°, and melts at 87—90° with decomposition.

F. S. K.

Action of Ammonia on the Compounds of Mercuric Cyanide with Metallic Chlorides. By R. Varet (*Compt. rend.*, **109**, 941—944).—Aqueous ammonia added to an aqueous solution of mercuric chlorocyanide gives a white precipitate of mercurammonium chloride, NH_2HgCl, and the solution contains mercuric cyanide and ammonium chloride. It follows that mercuric cyanide has no influence on the action of ammonia on mercuric chloride. If zinc cyanide is added to the solution of mercuric chlorocyanide which has been mixed with excess of ammonia, the precipitate redissolves, and when the liquid is concentrated over potash, the compound $HgCy_2,ZnCy_2,HgCl_2,4NH_3$ separates in nodules.

The action of a solution of dry ammonia in absolute alcohol on dry mercuric chlorocyanide at a low temperature yields a precipitate of the composition $HgCl_2,3NH_3$, and the liquid, when concentrated over potash, yields prismatic needles of the compound $HgCy_2,2NH_3$. The compound $HgCl_2,3NH_3$ alters rapidly when exposed to air and is decomposed by water.

The action of dry ammonia on dry mercuric chlorocyanide at 70° yields a greyish-white compound, $2Hg_2Cy_2Cl_2,3NH_3$, which is decom-

posed by water and by aqueous ammonia, and when heated yields a blackish powder.

Mercuric zinc chlorocyanide, $HgCy_2,ZnCy_2,HgCl_2 + 6H_2O$, in an aqueous solution, yields with ammonia a white precipitate of zinc cyanide and mercurammonium chloride, soluble in excess. When treated with dry ammonia, it loses water and combines with 4 mols. of ammonia. When treated with aqueous ammonia, it dissolves and the solution yields small, crystalline nodules of the compound $HgCy_2,ZnCy_2,HgCl_2,4NH_3$, which is decomposed by water, loses ammonia when exposed to the air, and is only slightly soluble in cold alcohol or cold aqueous ammonia.

Mercuric cupric chlorocyanide dissolves in aqueous ammonia, and when the liquid is concentrated, it yields blue, prismatic needles of the compound $2HgCy_2,CuCl_2,4NH_3$, which can be heated at 100° without loss of ammonia, and is only slightly soluble in cold, aqueous ammonia, but is decomposed by water.

Mercuric chlorocyanide alone is decomposed by ammonia, but in presence of another metallic cyanide a triple compound is formed and the decomposition of the mercuric salt is prevented.

C. H. B.

New Method of Preparing Potassium Ferricyanide. By G. KASSNER (*Chem. Zeit.*, **13**, 1701).—Recognising the unsatisfactory character of the methods employed for the conversion of potassium ferrocyanide into the ferricyanide, the author recommends the following:—

An aqueous solution of calcium plumbate is boiled with an alkaline carbonate; the precipitate, consisting of plumbic peroxide and calcium carbonate, converts ferrocyanide into ferricyanide. When carbonic anhydride is present to neutralise the base formed, the reaction is as follows:—$2K_4FeC_6N_6 + PbO_2(+ 2CaCO_3) + 2CO_2 = K_6Fe_2C_{12}N_{12} + K_2CO_3 + PbCO_3(+ 2CaCO_3)$. The ferricyanide and potassium carbonate are dissolved out, and the mixture of lead and calcium carbonates is reconverted into calcium plumbate by igniting in the air. The process, the author argues, is economical, inasmuch as there is no loss of material, and it amounts simply to utilising the atmospheric oxygen; moreover the bye-products are valuable, *e.g.*, caustic alkalis from the decomposition of the plumbate, and therefore it ought to tend towards the technical application of potassium ferricyanide (compare next abstract). D. A. L.

New Application of Potassium Ferricyanide. By G. KASSNER (*Chem. Zeit.*, **13**, 1302, 1338, 1407).—The author has observed that when alkaline potassium ferricyanide and hydrogen peroxide are mixed, oxygen is evolved, the former being converted into ferrocyanide; the following equations explain the change:—$K_6Fe_2C_{12}N_{12} + 2KHO = 2K_4FeC_6N_6 + H_2O + O$ and $O + H_2O_2 = H_2O + O_2$. The quantity of alkali regulates the reaction; therefore the following is suggested as a method for preparing oxygen:—Potassium ferricyanide dissolved in a little water is mixed with 3 per cent. hydrogen peroxide in a flask furnished with a delivery tube and a tap funnel down which the potash is delivered as quickly as desired. 58 grams

of ferricyanide and 100 c.c. of 3 per cent. hydrogen peroxide yield 2 litres of oxygen.

Alkaline carbonates also convert ferricyanide into ferrocyanide in the presence of hydrogen peroxide with the liberation of oxygen and carbonic anhydride, the carbonates being more active than the hydrogen carbonates. It is noteworthy that in these reactions there is no loss of valuable substance. Incidently it is noted that when ferricyanide is agitated and digested with about 20 per cent. potash and some milk of lime, oxygen is evolved, and the residue contains calcium hydroxide, some calcium carbonate, but no potassium ferrocyanide, inasmuch as the latter has become converted into a very sparingly soluble double ferrocyanide of potassium and calcium which adheres to the containing vessel. Potassium ferricyanide is to a great extent decomposed, when heated at 180° in a sealed tube with milk of lime and some potash, yielding ferric oxide, ammonia, potassium cyanide, and potassium ferrocyanide. D. A. L.

Ethereal Salts of Nitrous Acid. By G. BERTONI (*Gazzetta*, **18**, 431).—In continuation of his previous investigations (compare Abstr., 1886, 217 and 975, 1887, 458), the author has now prepared the following compounds, using the methods already described:—

Butyl nitrite, $C_4H_9{\cdot}NO_2$. A yellowish, mobile liquid of unpleasant odour. On inhalation, it produces the same symptoms as ordinary amyl nitrite. It is only very sparingly soluble in water, by which it is decomposed on prolonged contact, but dissolves in ether, chloroform, carbon bisulphide, &c.; it is insoluble in glycerol. It boils at 75° and its sp. gr. at 0° = 0·9114. It exhibits the general reactions of alcoholic nitrites.

Secondary butyl nitrite, $CHMeEt{\cdot}NO_2$, has the general properties of the alcoholic nitrites, and is insoluble in glycerol. It boils at 68°, and its sp. gr. at 0° = 0·8981.

Normal heptyl nitrite, $C_7H_{15}{\cdot}NO_2$, exhibits the same general reactions. It boils at 155°, and its sp. gr. at 0° = 0·8939. It is insoluble in glycerol. S. B. A. A.

First Oxide of the Pentahydric Alcohol from Diallyl Carbinol. By S. REFORMATSKY (*J. Russ. Chem. Soc.*, **21**, 295—319).—In order to obtain a pentatomic alcohol, the preparation of which was attempted in vain by Saytzeff and by Dieff, the author first treated diallyl carbinol with hypochlorous acid, and then decomposed the chlorhydrin thus obtained by potash (this vol., p. 120); the potash was then saturated with sulphuric acid or carbonic anhydride, and the water removed by evaporation. The alcoholic extract of the residue thus obtained was fractionally precipitated with ether in order to remove the salts and other impurities, and the alcohol-ether solution evaporated, when it yielded, not the alcohol required, but its oxide (first anhydride), $C_7H_{11}(OH)_3O$, as a viscid, sweet oil, which partly solidified to a crystalline mass after being kept two years. It is soluble in water and alcohol, insoluble in ether, and cannot be distilled without decomposition even under reduced pressure. The same product was formed on decomposing the chlorhydrin with lead oxide.

Dieff's triacetate was obtained by the action of acetic anhydride at 150°; the pentacetate and the pentabenzoate were also obtained in an impure condition. As regards the constitution of the anhydride in question, which is discussed by the author at some length, the conclusion is drawn that its formula is most probably:

$$CH(OH){<}{\begin{matrix}CH_2\cdot CH(OH)\cdot CH_2\\ CH_2\cdot CH(OH)\cdot CH_2\end{matrix}}{>}O.$$

The analogy between the constitution of this anhydride and that of the glucoses is not complete, as aniline has no action on it.

B. B.

First Oxide of a Tetrahydric Alcohol from Diallyl. By S. Reformatsky (*J. Russ. Chem. Soc.*, **21**, 320—326).—The author, on attempting to obtain a tetratomic alcohol from diallyl, by first converting it into the chlorhydrin, $C_6H_{10}(OH)_2Cl_2$, by means of hypochlorous acid, and then acting on this with potash, obtained only the same oxide, $C_6H_{10}O(OH)_2$, as Přibytek. This, however, is not converted into the alcohol by assimilation of the elements of water, as stated by Přibytek. After studying the acetate, and comparing the properties of the oxide with those of the pentatomic alcohol described in the preceding abstract, the author concludes that the substance in question has the constitution: $\begin{matrix}CH_2\cdot CH(OH)\cdot CH_2\\ | \\ CH_2\cdot CH(OH)\cdot CH_2\end{matrix}{>}O.$ B. B.

Dehydration of Monhydric Alcohols. By A. Volkoff. (*J. Russ. Chem. Soc.*, **21**, 327—341).—From experiments on the dehydration of a series of saturated monhydric alcohols the author draws the following conclusions. Heating the alcohols to a high temperature alone (up to 253° and in some cases to 310°) does not give rise to dehydration, but it remains an open question whether this effect is not produced in some cases by heating to 400° or higher. On heating secondary and tertiary alcohols with a small quantity of methyl iodide, however, complete decomposition takes place, whereas primary alcohols are converted into simple ethers containing the radicle of the primary alcohol; one of the first phases of the reaction being the formation of the corresponding iodide. This conversion is either represented by the equation: $mC_nH_{2n+1}\cdot OH + MeI = C_nH_{2n+1}I + Me\cdot OH + (m-1)C_nH_{2n+1}\cdot OH$, or the compound methyl ether is first formed together with hydrogen iodide, which in the second phase of the reaction gives the alkyl iodide:

$$\text{(I)}\ m(C_nH_{2n+1}\cdot OH) + MeI = Me\cdot O\cdot C_nH_{2n+1} + (m-1)C_nH_{2n+1}\cdot OH + HI$$

and

$$\text{(II)}\ (m-1)C_nH_{2n+1}\cdot OH + HI = C_nH_{2n+1}I + (m-2)C_nH_{2n+1}\cdot OH + H_2O.$$

The further progress of the reaction is dependent on the stability of the iodide formed under the conditions of the experiment, so that secondary and tertiary iodides are decomposed, yielding the hydrocarbons of the ethylene series and hydrogen iodide, whereas the primary iodides react with a molecule of the alcohol present in excess,

forming the simple ether thus: $C_nH_{2n+1}I + C_nH_{2n+1}OH = (C_nH_{2n+1})_2O + HI$. The hydrogen iodide thus produced again gives rise to the formation of a fresh molecule of the iodide, and the reaction proceeds continuously in this way, until all the alcohol is converted, and at last free hydrogen iodide remains. The author is about to publish an account of similar experiments with unsaturated alcohols. B. B.

β-Inosite. By MAQUENNE (*Compt. rend.*, **109**, 968—970).—If heated at 160—170° with saturated hydriodic acid in presence of some red phosphorus, β-inosite yields a phenol which, when treated with iodine and potassium hydroxide, yields an insoluble iodo-derivative. The latter crystallises from alcohol or chloroform in slender, yellowish needles, soluble in alkalis, but insoluble in water and dilute acids. With nitric acid it yields trinitrophenol, and hence is identical with the product obtained from inosite under the same conditions. This result and the fact that it yields quinones on oxidation prove that β-inosite has the same formula as ordinary inosite. The absence of aldehydic or ketonic groups is proved by the absence of reducing power and the non-formation of any compound with phenylhydrazine acetate.

Hexacetyl-β-inosite, $C_6H_6(OAc)_6$, obtained by the action of acetic anhydride in presence of zinc chloride, could not be obtained in crystals. It is very fusible, and even volatile, dissolves in alcohol and ether, but is insoluble in water.

Hexabenzoyl-β-inosite, obtained by the action of benzoic chloride in presence of small quantities of zinc, crystallises from amyl alcohol in brilliant, white needles which melt at 253°, and are insoluble in most solvents in the cold, although somewhat soluble in hot amyl alcohol.

β-Inosite, in a 10 per cent. solution at 14·3°, has a rotatory power $[\alpha]_D = 65·0°$, almost identical with that of β-pinite. It differs in the physical and chemical properties of itself and its derivatives from ordinary inosite, the quebrachite of Tauret, and the matezo-dambose of A. Girard.

It follows from these and the previous results that pinite is the mono-methyl ether of β-inosite, and is, therefore, isomeric with bornesite and quebrachite. C. H. B.

Rhamnodiazine. By B. RAYMAN and O. POHL (*Ber.*, **22**, 3247—3249; compare Abstr., 1889, 485).—Rhamnodiazine is decomposed when boiled with methyl iodide in methyl alcoholic solution, yielding methylamine and brown, amorphous substances. It is decomposed by glacial acetic acid with liberation of rhamnose. A crystalline compound is obtained when rhamnodiazine is treated with hydrogen chloride in alcoholic solution, but it cannot be easily separated from the ammonium chloride, which is also formed in the reaction; it has probably the composition $C_{14}H_{22}N_2O_7,2HCl$.

When rhamnose, in alcoholic solution, is treated at the ordinary temperature with ethyl acetoacetate (1 mol.), and an amido-compound (2 mols.) such as aniline, toluidine, β-naphthylamine, or ethyl imidocrotonate, α-rhamnosamine is formed.

Rhamnodiazine probably has the constitution—

$C_5H_{11}O_4\cdot CH(N\colon CMe\cdot CH_2\cdot COOEt)_2$. F. S. K.

Melitose. By BERTHELOT (*Bull. Soc. Chim.* [3], 2, 655—657; compare Abstr., 1886, 138).—Melitose (raffinose) obtained from cotton-cake separates from alcohol in small, hard, granular crystals, having the formula $C_{36}H_{64}O_{32} + 10H_2O$, but when crystallised from aqueous alcohol yields lamellar crystals of $C_{36}H_{64}O_{32} + 12H_2O$; the rotatory power being the same for both hydrates.

Good beer yeast determines the total fermentation of melitose; with feeble baker's yeast, a complete arrest of fermentation occurs after 48 hours, and a residue of carbohydrate amounting to 67—75 per cent. of the original melitose remains. In one instance, 100 parts of melitose, fermented with a feeble yeast, yielded carbonic anhydride, 15·6, alcohol, 16, and residual carbohydrates, 74·3 parts, of which 30 per cent. is reducing sugar.

The ferment probably causes a prior hydrolysis of melitose to a glucose and either a reducing saccharose or two glucoses, of which but one is reducing. T. G. N.

An Unfermentable, Dextrorotatory Constituent of Honey. By E. v. RAUMER (*Zeit. ang. Chem.*, 1889, 607—609).—Sieben has stated that the presence of starch-sugar in honey can be detected by means of its unfermentable dextrin, since, according to his experiments, honey contains no substance which could be mistaken for it. The author has, however, recently, examined a number of specimens of honey, including several which were unquestionably genuine, and they all, after fermentation, exhibited dextrorotation. Some of the active substance was prepared in a state of approximate purity by precipitation with alcohol and washing with ether. It appears to belong to the class of dextrins, and different preparations showed a specific rotatory power of 52° to 68°, which, by inversion, was diminished to about half. The reducing power of two different preparations was respectively 0·455 and 0·304 of copper for 1 part of substance: by inversion this was increased in the ratio of 2·7 : 1. After inversion the substance fermented completely, its rotatory power diminishing during the fermentation, but always remaining positive, whence it is inferred that lævulose is not present.

M. J. S.

Allyltrimethylammonium Compounds. By A. PARTHEIL (*Ber.*, 22, 3317—3324).—Weiss has described (*Chem. Centr.*, 1887, 1345) the tribromide, $C_3H_5Br_2\cdot NMe_3Br$, of this base. When this derivative is treated with alcoholic potash or fresh silver oxide, *bromallyltrimethylammonium bromide*, $C_3H_4Br\cdot NMe_3Br$, is formed. This salt crystallises in colourless prisms, soluble in water, alcohol, and warm chloroform, insoluble in ether, and melts at 165°. The *platinochloride* forms easily soluble, reddish-brown plates melting with decomposition at 220°; the *aurochloride*, sulphur-yellow crystals melting at 181°. With excess of bromine it yields *bromallyldibromide-trimethylammonium bromide*, $CHBr_2\cdot CHBr\cdot CH_2\cdot NMe_3Br$, which crys-

tallises in colourless scales and melts at 156°. When the monobromo-bromide is further treated with alcoholic potash, *trimethyltrimethineammonium bromide*, $NMe_3Br\cdot CH<\begin{matrix}CH\\ \|\\ CH\end{matrix}$, is formed, which is not soluble in chloroform, and yields the free *base* when digested with excess of alcoholic potash. The *aurochloride* forms yellow scales. No platinochloride could be obtained, as it was so easily reducible; the aurochloride deposited gold when boiled with water. When the bromide is treated with excess of bromine, it yields a *perbromide* crystallising in dark, yellowish-brown plates; when this is boiled with absolute alcohol, it is converted into the *base*

$$OH\cdot NMe_3\cdot CH<\begin{matrix}CHBr\\ |\\ CHBr\end{matrix},$$

crystallising in colourless needles, and melting at 187°. The *platinochloride* forms brownish-red plates melting at 232°, the *aurochloride*, citron-yellow plates melting at 193°. When boiled with silver nitrate, the bromide yielded the compound $C_3H_3Br_2\cdot NMe_3\cdot NO_3$.

When allyltrimethylammonium iodide is treated with hydriodic acid at 100°, *γ-moniodopropyltrimethylammonium iodide*, $C_3H_6I\cdot NMe_3I$, is formed. This crystallises in colourless needles soluble in water and alcohol, and melts at 151°. The *platinochloride*, $(C_3H_6I\cdot NMeCl)_2,PtCl_4$, forms reddish-yellow needles, and melts with decomposition at 237°; the *aurochloride*, brownish-yellow scales, and melts at 135°. When boiled for some time with silver nitrate, the iodide yields γ-homocholine. Hydrobromic and hydrochloric acids, at about 160—170°, yield similar additive-products, but these were not obtained pure; the *platinochloride*, $(C_3H_6Cl\cdot NMe_3Cl)_2,PtCl_4$, crystallises in dark, brownish-red needles; the *aurochloride* in golden-yellow plates melting at 185°.

Hypochlorous acid forms two isomeric additive-products with allyltrimethylammonium chloride. The first yields a sparingly soluble *platinochloride*, $(OH\cdot C_3H_5Cl\cdot NMe_3Cl)_2,PtCl_4$, crystallising in yellow scales melting at 234—235°, and a moderately soluble *aurochloride*, crystallising in yellow plates, melting at 162°. When heated with silver oxide, the compound, $NMe_3Cl\cdot CH\cdot CH<\begin{matrix}O\\ |\\ CH_2\end{matrix}$, is formed, which crystallises in yellowish-red, easily soluble, octohedral needles, and melts at 207°. The second isomeride forms an easily soluble *platinochloride*, crystallising in yellowish-red needles melting with decomposition at 225—226°, and an easily soluble *aurochloride* melting at 192°. L. T. T.

Ketoaldehydes. By L. CLAISEN and L. MEYEROWITZ (*Ber.*, **22**, 3273—3281; compare Abstr., 1889, 619).—*Formyldiethyl ketone* (*propionylpropionaldehyde*), COEt·CHMe·COH, is prepared by gradually adding a well-cooled mixture of ethyl formate (11 grams) and diethyl ketone (13 grams) to finely-divided sodium ethoxide (10·5 grams), covered with dry ether (10 parts). After keeping for 12 hours, the sodium-derivative (about 12 grams) is separated by filtration, dis-

solved in ice-cold water, the solution acidified with hydrochloric acid, and the oil extracted with ether; the crude product is purified by distillation under reduced pressure (45—50 mm.). It forms colourless crystals, melts at about 40°, boils at 75—85° (45—50 mm.), and dissolves freely in water and the ordinary organic solvents. It has a peculiar odour, recalling that of the fatty aldehydes, and also that of ethyl acetoacetate. When exposed to the air, the crystals turn reddish-brown, and slowly deliquesce. In alcoholic solutions, ferric chloride produces an intense dark-violet coloration. When heated in small quantities, it distils without decomposition at 164—166°, under the ordinary pressure.

The *ammonium*-derivative, $C_6H_9O_2{\cdot}NH_4$, separates in colourless, very deliquescent crystals when ammonia is passed into an ethereal solution of the ketoaldehyde. The *copper* compound, $(C_6H_9O_2)_2Cu$, separates as a green precipitate when copper acetate is added to an alcoholic solution of the ketoaldehyde; it dissolves freely in alcohol and warm benzene, but on adding light petroleum to the benzene solution, it is reprecipitated in greyish-green needles melting at 167—168°. A compound, of the composition $C_{12}H_{14}N_2$, most probably methylethylphenylpyrazole, is formed when the ketoaldehyde is treated with phenylhydrazine; it is a colourless liquid with an odour of quinoline, boils at 282—284°, and has a sp. gr. = 1·0476 at 15°. This compound is isomeric with the propylphenylpyrazole prepared from methyl propyl ketone, ethyl formate, and phenylhydrazine (Abstr., 1888, 671).

Formylethyl phenyl ketone (*benzoylpropaldehyde*), COPh·CHMe·COH, is prepared from phenyl ethyl ketone, as described in the case of the preceding compound, but as the sodium-derivative of the ketoaldehyde cannot easily be separated by filtration, the whole of the product of the reaction is treated with ice-cold water; the supernatant ethereal solution then separated, the residual alkaline solution acidified with hydrochloric acid, and the precipitate recrystallised from dilute alcohol. The ethereal solution contains about 50 per cent. of the phenyl ethyl ketone employed; if this unchanged ketone is treated again with ethyl formate and sodium ethoxide, 51 grams of the ketoaldehyde can be obtained from 54 grams of the ketone. Formylethyl phenyl ketone crystallises from alcohol in slender, colourless needles, melts at 118—119°, and is readily soluble in alcohol, benzene, methyl alcohol, and ethyl acetate, and moderately easily in ether, carbon bisulphide, and hot water, but only very sparingly in light petroleum. In alcoholic solutions, ferric chloride produces a dark-violet coloration, and copper acetate an olive-green, crystalline precipitate. It dissolves freely, and without change, both in alkalis and in alkaline carbonates. The *anilide*, COPh·CHMe·CH:NPh, prepared by heating the ketoaldehyde with aniline at 150°, crystallises in colourless needles, melts at 132°, and dissolves freely in ether, but is reprecipitated on adding light petroleum.

Formylpropyl phenyl ketone (*benzoylbutaldehyde*), COPh·CHEt·COH, crystallises from hot dilute alcohol in colourless plates, melts at 86—87°, and shows the same behaviour with ferric chloride, copper acetate, alkalis, and alkaline carbonates as the preceding compound.

The *anilide*, $C_{17}H_{17}ON$, crystallises in colourless needles, melts at 120°, and gradually decomposes on keeping.

Formyldeoxybenzoïn (*benzoylphenylacetaldehyde*), COPh·CHPh·COH, forms yellow crystals, melts at 110°, and is readily soluble in alkalis and moderately easily in alkaline carbonates. It gives a dark-violet coloration with ferric chloride, and a light-green copper-derivative with copper acetate.

Phenyl isopropyl ketone does not react with ethyl formate and sodium ethoxide; the behaviour of a ketone under these conditions may serve as a means of ascertaining its constitution by determining whether the carbonyl-group is in direct combination with a primary radicle on the one hand, or with a secondary or tertiary radicle on the other.

Experiments lately carried out seem to show that camphoraldehyde (Abstr., 1889, 619) has probably the constitution $C_8H_{14}<\begin{matrix}C\!:\!CH\cdot OH \\ | \\ CO\end{matrix}$, and is not a true aldehyde; if this is really the case, the ketoaldehyde described above have probably an analogous constitution,

R·CO·CR:CH·OH. F. S. K.

Symmetrical Tetrabromodiacetyl. By H. F. KELLER (*Ber.*, **23**, 35—37).—When diacetyl is treated with bromine in carbon bisulphide solution, the reaction does not, as previously stated (Abstr., 1889, 491), stop with the formation of a dibromo-derivative, but proceeds further, although somewhat slowly, the final product being *tetrabromodiacetyl*, $CHBr_2\cdot CO\cdot CO\cdot CHBr_2$. This crystallises from carbon bisulphide in large, transparent, yellow tablets, which melt at 95—96°. It strongly resembles in all its properties the tetrachlorodiacetyl obtained by Levy and Jedlicka (Abstr., 1888, 444; see also this vol., p. 232) by the action of hydrochloric acid and potassium chlorate on chloranilic acid. Like this compound, it dissolves in ether, chloroform, and benzene, forming a yellow solution, but gives a colourless solution in hot water, and is readily attacked by aqueous soda. It also unites with phenylhydrazine in alcoholic solution, forming a compound, $C_{16}H_{14}Br_2N_4O$, which crystallises from benzene in cinnabar-red, granular crystals. These become brown at 185°, and melt with decomposition at 190°.

The striking analogy between the tetrabromo-derivative and Levy and Jedlicka's compound, removes the last doubts as to the correctness of the constitution assigned to the latter substance. H. G. C.

Decomposition of Acetic Anhydride by Water. By N. MENSHUTKIN and M. VASILIEFF (*J. Russ. Chem. Soc.*, **21**, 188—198).—The aim of the present investigation was to collect experimental material in reference to the hydration of organic anhydrides. The first member of the compounds in question is acetic anhydride, and the authors attempted to find the constant of velocity of its hydration. Although a great many experimental data are given in the form of tables, they are not suited for abstraction, and the result of

the investigation is that the authors did not succeed in solving the problem in question, the difficulty being that the two substances do not mix in all proportions, and no solvent could be found which did not act either on the substances themselves or on the products of the reaction. In order to give a rough idea of some of the reactions of hydration, a table is given of the decomposition of acetic anhydride, acetamide, and ethyl acetate by 1 mol. of water at 100° under the same conditions. The experiments were made in the presence of acetic acid, however, for the reason stated above.

Substance.	Acetic anhydride $+ 1H_2O$.	Acetamide $+ 1H_2O$.	Ethyl acetate $+ 1H_2O$.
Acetic acid added..	11·86 p. c.	15·85 p. c.	11·45 p. c.
	Decomposition in percents.		
Time.			
1 min.	25·68	4·51	0·2
11 ,,	83·9	4·64	0·5
61 ,,	98·5	4·94	0·87
121 ,,	99·5	5·82	0·99
181 ,,	99·7	6·41	—

It is seen from an inspection of this table that acetic anhydride is almost completely decomposed after one hour; whereas the decomposition of acetamide is very small, and that of ethyl acetate has scarcely begun. B. B.

γ-Amidobutyric Acid. By S. Gabriel (*Ber.*, **22**, 3335—3339).—Attempts to obtain the compound $C_8H_4O_2\!:\!N\cdot CH_2\cdot CH_2\cdot CH_2\cdot CN$ by the action of potassium or mercuric cyanide on bromopropylphthalimide proved fruitless. *γ-Bromobutyronitrile*, $CH_2Br\cdot CH_2\cdot CH_2\cdot CN$, was obtained by mixing 200 grams of trimethylene bromide with 60 grams of potassium cyanide in aqueous solution and enough alcohol to cause mixture of the layers, and then allowing the whole to remain for 14—16 hours at 40°. It is a heavy oil boiling at 205°. When this substance is heated at 150° with potassium phthalimide in molecular proportion, it yields the sought-for *γ-cyanopropylphthalimide*,

$$C_8H_4O_2\!:\!N\cdot C_3H_6\cdot CN.$$

This is also produced when γ-chlorobutyronitrile is substituted for the bromine-compound. It forms transparent, colourless, rhombic crystals melting at 80·5—81·5°. It is soluble in the usual solvents when hot. When digested for three hours with 27 per cent. hydrochloric acid, it is resolved into phthalic acid and *γ-amidobutyric acid*, $NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOH$. The latter crystallises in snow-white scales soluble in alcohol and water, melts at 183—184°, and begins to lose water at the same temperature; if the heating is continued for some time at 200°, *pyrrolidone*, $NH{<}{\begin{matrix}CH_2\cdot CH_2\\ CO\cdot CH_2\end{matrix}}$, is formed. This forms a colourless, fibrous, crystalline mass melting at 25—28°, and having an odour resembling that of acetamide. It is very soluble in

water, the solution reacting neutral and yielding a crystalline *platinochloride* and *aurochloride*. When exposed to moist air, the crystals first deliquesce, and the liquid afterwards again solidifies to rhombic or hexagonal plates of the *hydrate* $C_4H_7NO + H_2O$, which melts at 35° and is isomeric, not identical with the acid.

γ-Amidobutyric acid is probably identical with Schotten's piperidinic acid (Abstr., 1883, 813). L. T. T.

Thio-derivatives of the Crotonic Acids. By W. AUTENRIETH (*Annalen*, **254**, 222—252).—*β-Thiophenylcrotonic acid*, $\begin{array}{c}\mathrm{SPh{\cdot}C{\cdot}Me} \\ \| \\ \mathrm{H{\cdot}C{\cdot}COOH}\end{array}$, is obtained when the sodium salt of chlorocrotonic acid (m. p. 94·5°) is treated with sodophenylmercaptide, as described by Escales and Baumann (Abstr., 1886, 878) in the preparation of β-thiophenylisocrotonic acid. The yield is almost quantitative. It melts at 157—158° yielding carbonic anhydride and β-thiophenylpropylene (b. p. 207—208°), identical with the compound obtained by Escales and Baumann. It is readily soluble in hot alcohol, ether, chloroform, and light petroleum, and in other respects behaves like the isomeride referred to above. The salts of the alkalis and alkaline earths are readily soluble in water. The *barium* salt, $(C_{10}H_9SO_2)_2Ba + H_2O$, crystallises in colourless plates or needles. The *silver*, *mercury*, and *lead* salts are amorphous.

β-Thioethylisocrotonic acid, $\begin{array}{c}\mathrm{Me{\cdot}C{\cdot}SEt} \\ \| \\ \mathrm{H{\cdot}C{\cdot}COOH}\end{array}$, prepared by treating β-chlorisocrotonic acid with sodioethylmercaptide, separates from alcohol in well-defined crystals, melts at 91—92° with evolution of carbonic anhydride, and is readily soluble in chloroform, ether, benzene, and light petroleum, but almost insoluble in boiling water. It gives a dark-green coloration when warmed with isatin and sulphuric acid, and behaves in other respects like the corresponding phenyl-componnds. The salts of the alkalis and alkaline earths are very readily soluble in water. The *silver* salt is readily soluble in water, but it is decomposed when the solution is boiled. The *barium* salt $(C_6H_9SO_2)_2Ba + H_2O$, crystallises from water in thin plates.

β-Thioethylcrotonic acid, $\begin{array}{c}\mathrm{SEt{\cdot}C{\cdot}Me} \\ \| \\ \mathrm{H{\cdot}C{\cdot}COOH}\end{array}$, prepared from chlorocrotonic acid (m. p. 94·5°) in like manner, separates from water in well-defined crystals, melts at 112—113° with evolution of carbonic anhydride, and resembles the preceding compound in its behaviour and properties. The *barium* salt crystallises with 2 mols. H_2O; the other salts resemble generally those of the isomeric acid, except that the *silver* salt is not decomposed by boiling water.

β-Thioethylpropylene, $SEt{\cdot}CMe{:}CH_2$, prepared by heating either of the thioethylcrotonic acids above its melting point, is a colourless, disagreeably smelling oil boiling at 109—110°; it gives a green coloration when warmed with isatin and sulphuric acid.

β-Phenoxycrotonic acid, $\begin{array}{c}\mathrm{Me{\cdot}C{\cdot}OPh} \\ \| \\ \mathrm{H{\cdot}C{\cdot}COOH}\end{array}$, is obtained by heating sodium β-chlorisocrotonate with sodium phenoxide at about 130°, or by heating

sodium β-chlorocrotonate with sodium phenoxide at about 180°. It separates from light petroleum in well-defined crystals, melts at 149—150° with decomposition, and is readily soluble in ether, alcohol, and chloroform, but only sparingly in boiling water. It is readily decomposed with liberation of phenol, so that it gives the characteristic reactions of phenols.

β-Phenoxypropylene, OPh·CMe:CH$_2$, prepared by heating the preceding compound above its melting point, is a colourless, pleasant smelling oil boiling at 160—162°. It is not decomposed when boiled with water or when distilled with concentrated potash. It gives a red coloration when boiled with Millon's reagent, and a yellow brominated derivative when treated with bromine.

α-Thiophenylcrotonic acid, $\begin{array}{c}\text{H·C·Me}\\ \Vert\\ \text{SPh·C·COOH}\end{array}$, can be easily prepared from the sodium salt of α-chlorocrotonic acid (m. p. 97°), as described in the case of the corresponding β-compound. It separates from water in long needles, and from alcohol in well-defined crystals, melts at 86°, and decomposes at 145—150° with evolution of carbonic anhydride. It is readily soluble in ether, chloroform, and alcohol, but only sparingly in cold light petroleum, and is almost insoluble in cold water. It is much more stable than the corresponding β-acid, and when heated with concentrated hydrochloric acid or with potash, it yields only a trace of mercaptan. When warmed with concentrated sulphuric acid, it gives a cherry-red coloration. The salts of the alkalis are soluble in water and alcohol. The *potassium* salt forms colourless, deliquescent crystals. The salts of the alkaline earths are readily soluble in water and do not crystallise readily. The *mercury*, *copper*, and *silver* salts are soluble in boiling water.

α-Thiophenylisocrotonic acid, $\begin{array}{c}\text{Me·C·H}\\ \Vert\\ \text{SPh·C·COOH}\end{array}$, prepared from α-chlorisocrotonic acid (Wislicenus, Abstr., 1887, 665), crystallises from water in nacreous plates, melts at 80°, and decomposes at 160—165° with evolution of carbonic anhydride. It is very readily soluble in alcohol, ether, and chloroform, but almost insoluble in cold water. The salts resemble those of the isomeric acid.

α-Thiophenylpropylene is formed when either of the α-thiophenylcrotonic acids is distilled; it is a colourless oil insoluble in water. The compound obtained from the iso-acid boils at 220—228°, that obtained from α-thiophenylcrotonic acid at 217—223°, but otherwise no marked difference between the two substances was observed.

The two thioethylcrotonic acids, prepared by treating the two α-chlorocrotonic acids with sodioethylmercaptide in alcoholic solution, are oily liquids which show no difference in behaviour or in properties.

F. S. K.

Linoleïc Acid. By A. Reformatsky (*J. Russ. Chem. Soc.*, **21**, 202—226).—Linoleïc acid was subjected to a most careful purification, and then to elementary analysis, in order to find its true formula; but no satisfactory results could be obtained owing to the rapid oxidation of the acid by atmospheric oxygen. The acid cannot

be distilled under reduced pressure without undergoing a thorough change. Subsequent researches, especially the analysis of its derivatives, have shown, however, that its formula is not $C_{16}H_{28}O_2$, as hitherto assumed, but that it consists principally of the compound $C_{18}H_{32}O_2$; for the ethyl salt is $C_{17}H_{31}O{\cdot}OEt$, and from this the pure acid can be obtained by saponification and subsequent decomposition of the alkali salt with dilute sulphuric acid.

The additive-product with iodine has the formula $C_{18}H_{32}O_2I_4$, but it could not be isolated; that with bromine is $C_{18}H_{32}O_2Br_4$; the hexabromide, $C_{18}H_{30}O_2Br_6$, therefore, is partly a product of substitution. Oxidation with alkaline permanganate yielded *tetrahydroxystearic acid*, $C_{18}H_{32}O_2(OH)_4$, the four hydroxyl-groups being added on at the two double unions. In addition to this, azelaic and formic acids were also formed. The dihydroxystearic acid obtained at the same time is probably due to the presence of some oleïc acid. Hazura's "linolenic" and "isolinolenic" acids could not be found among the products of oxidation. It remains an open question, therefore, whether linoleïc acid is really a heterogeneous substance, as Hazura states it to be. B. B.

Monosubstituted Succinic Acids. By R. Anschütz and C. Bennert (*Annalen*, **254**, 155—168; compare Abstr., 1885, 1049).—Chlorosuccinic acid yields fumaric acid when it is boiled with water. Methyl chlorosuccinate boils at 220·8° (772·5 mm.) without decomposition; methyl bromosuccinate is decomposed into methyl fumarate and hydrogen bromide when it is distilled under the ordinary pressure.

Monochloro- and monobromo-succinic anhydrides are decomposed when distilled under the ordinary pressure, yielding maleïc anhydride and the halogen acid. Dimethyl levomalate is easily decomposed by water; when distilled under the ordinary pressure, it gives methyl fumarate and water.

Acetylmalic acid, prepared by treating acetylmalic anhydride with the theoretical quantity of water, is a colourless, crystalline compound, melts at 132°, and is decomposed by warm water. The methyl salt yields acetic acid and methyl fumarate when it is distilled under the ordinary pressure. F. S. K.

Isomerism of Maleïc and Fumaric Acid. By R. Anschütz (*Annalen*, **254**, 168—182; compare Abstr., 1887, 916, and 1888, 448).—The author does not agree with Wislicenus in the view that maleïc acid and fumaric acid are stereochemically isomeric, and he points out that Wislicenus' explanation of the conversion of maleïc into fumaric acid by hydrochloric acid is not in accordance with experiment, since the change is brought about by concentrated hydrochloric acid at a temperature (about 10°) at which chlorosuccinic acid is not changed by hydrochloric acid. The fact that chlorosuccinic anhydride does not yield fumaric acid when treated with water is also evidence against Wislicenus' assumption that chlorosuccinic acid is an intermediate product in the conversion of maleïc into fumaric acid. F. S. K.

Ethyl Methylenemalonate and its Polymeride. By N. Zelinsky (*Ber.*, **22**, 3294—3302).—A polymeride of ethyl methylenemalonate, $CH_2:C(COOEt)_2$, is obtained when ethyl malonate (16 grams) is treated with methylene iodide (26·8 grams) and sodium ethoxide (= 4·6 grams of sodium) in alcoholic solution. After boiling for about 10 hours, water is added, the precipitated oil extracted with ether, and the unchanged methylene iodide and ethyl malonate removed by distilling with steam. The residual oil has the composition $C_8H_{12}O_4$; when it is submitted to fractional distillation under reduced pressure (120—130 mm.), it can be separated into a solid, amorphous substance and a thick, oily liquid of higher boiling point, both of which have, however, the same percentage composition.

The solid compound is a colourless, odourless, paraffin-like substance, which melts at 155—156°, and boils at about 225—235° (120—130 mm.). It is rather sparingly soluble in ether, benzene, and alcohol, and almost insoluble in water. A molecular weight determinatiou by Raoult's method in glacial acetic acid solutiou showed that it has the molecular formula $C_{16}H_{24}O_8$. When it is heated, it gives off heavy vapours, which have a most irritating odour, and on further heating it distils at about 290—300° under the ordinary pressure, seemingly without decomposition, yielding a heavy, oily distillate with an irritating odour; this distillate gradually solidifies when kept over sulphuric acid, but it retains its sharp smell.

If the product of the action of methylene iodide on ethyl sodiomalonate is distilled under the ordinary pressure, a considerable quantity passes over between 120° and 210°. This fraction is a mobile oil with an irritating odour; it can be kept under water for a long time without undergoing polymerisation, and when treated with bromine it is converted into a compound of the composition $C_8H_{12}Br_2O_4$. This additive-product is a yellow, sharp-smelling oil, and boils at 185—190° (75—85 mm.) with slight decomposition. When kept for some time, it deposits a crystalline compound which has not yet been investigated.

When the solid polymeride (m. p. 155—156°) referred to above is hydrolysed with potash, it is converted into an acid, the calcium salt of which is much more readily soluble in cold than in hot water. This salt seems to have the composition $C_4H_4O_5Ca$. When an aqueous solution of the acid is kept over sulphuric acid, a thick, gummy mass is obtained, and finally a small quantity of a crystalline compound is deposited. F. S. K.

Circular Polarisation of certain Tartrate Solutions. By J. H. Long. See this vol, p. 313.

Conversion of Ethyl Acetoneoxalate into Symmetrical Hydroxytoluic Acid. By L. Claisen (*Ber.*, **22**, 3271—3273).—The acid (m. p. 90°) previously described (Claisen and Stylos, Abstr., 1887, 917), which is obtained from ethyl sodacetoneoxalate (ethyl sodacetylpyruvate), has the molecular formula $C_{12}H_{16}O_8$. An analogous compound of the composition $C_{11}H_{14}O_8$ can be obtained in like manner from methyl sodacetoneoxalate. Both these substances act

like monobasic acids, and form normal salts with alkalis and with barium. The aqueous solutions of these salts are colourless, but become golden-yellow on adding an alkali or baryta, owing to the formation of a basic salt. When a solution of the acid in excess of baryta is warmed, barium oxalate is precipitated in considerable quantity, and the solution contains the salt of hydroxytoluic acid [Me : OH : COOH = 1 : 3 : 5].

The compound $C_{12}H_{16}O_8$ is an ethyl hydrogen salt formed from ethyl acetoneoxalate according to the equation $2COMe\cdot CH_2\cdot CO\cdot COOEt + H_2O = COMe\cdot CH_2\cdot C(OH)(COOH)\cdot CHAc\cdot CO\cdot COOEt + C_2H_5\cdot OH$. When warmed with excess of baryta, it is probably decomposed into oxalic acid and diacetoneoxalic acid, $(COMe\cdot CH_2)_2{:}C(OH)\cdot COOH$, and the latter is then converted into hydroxytoluic acid according to the equation $(COMe\cdot CH_2)_2{:}C(OH)\cdot COOH = C_8H_8O_3 + 2H_2O$.

F. S. K.

Acetyltrichlorophenomalic Acid. By R. ANSCHÜTZ (*Annalen*, **254**, 152—154; compare Abstr., 1887, 916).—*Acetyltrichlorophenomalic acid*, $CH{<}{\begin{matrix}CH\cdot C(OAc)\cdot CCl_3\\ CO\cdot O\end{matrix}}$, is readily obtained by heating trichlorophenomalic acid for half an hour at 100° with excess of acetic anhydride. It crystallises from dilute alcohol in colourless prisms, melts at 86°, and is very readily soluble in glacial acetic acid, ether, benzene, and chloroform, and readily in alcohol. It is not changed by boiling water, but it is decomposed by boiling baryta-water, with formation of chloroform, acetic acid, and maleïc acid. The formation and behaviour of this compound are in accordance with the author's views that trichlorophenomalic acid has the constitution $CH{<}{\begin{matrix}CH\cdot C(OH)\cdot CCl_3\\ CO\cdot O\end{matrix}}$.

F. S. K.

Formation of Hydantoïn. By R. ANSCHÜTZ (*Annalen*, **254**, 258—261).—Hydantoïn is formed when sodium dihydroxytartrate (10 grams) is rubbed to a paste with carbamide (5 grams) and 25 per cent. hydrochloric acid (12 c.c.), and the mixture warmed to 50—60°. The crude substance which separates from the filtered solution can be easily obtained in a pure condition by recrystallisation; it melts at 215—216°.

F. S. K.

Chlorobenzenes obtained from Anisoïl. By L. HUGOUNENQ (*Bull. Soc. Chim.* [3], **2**, 603—605).—Chlorine (1200 grams) is passed into anisoïl (108 grams) containing iodine (2·5 grams), the flask being heated from 60° to 230° as chlorination progresses. The product, after cooling, washing, and crystallisation from a hot mixture of equal parts of benzene and alcohol, yields hexachlorobenzene, pentachlorobenzene, and 1 : 2 : 4 : 5-tetrachlorobenzene. From the mother liquor, an oil boiling at 247—250° separates, which appears to be a mixture of tetrachlorobenzene and trichlorobenzene. The gas evolved in the reaction is carbon oxychloride.

T. G. N.

Derivatives of Bromothymol. By G. MAZZARA (*Gazzetta*, **18**, 514.—*Benzoylbromothymol*,

$$C_6H_2BrMePr{\cdot}OBz\ [Me : OBz : Pr : Br = 1 : 3 : 4 : 6].$$

To prepare this compound, thymol is mixed with an equal amount of benzoic chloride, and heated first on the water-bath, and then on the oil-bath at 160—180° in a reflux apparatus under an additional pressure of $\frac{1}{3}$ atmosphere, until hydrogen chloride ceases to come off. The product is cooled in a stream of carbonic anhydride, dissolved in carbon bisulphide which has been freshly dehydrated with phosphoric anhydride, and bromine added in molecular proportion to the thymol originally taken. The whole is then allowed to remain for 24 hours in order that the carbon bisulphide may evaporate spontaneously.

On recrystallising the residue from alcohol, after washing it with water and pressing, the benzoylbromothymol is obtained in white, lustrous needles which melt at 65—66°. From light petroleum it separates in large, colourless crystals which melt at 66—68°.

Acetylbromothymol,

$$C_6H_2BrMePr{\cdot}OAc\ [Me : OAc : Pr : Br = 1 : 3 : 4 : 6],$$

is prepared from acetic chloride and bromothymol. When freshly prepared, it is a transparent, colourless liquid, which acquires a reddish tinge on exposure to light. It becomes syrupy at low temperatures, and is decomposed by potash.

Methylbromothymol,

$$C_6H_2BrMePr{\cdot}OMe\ [Me : OMe : Pr : Br = 1 : 3 : 4 : 6],$$

is obtained on heating a mixture of the proper quantities of methyl iodide and of a solution of bromothymol in methyl alcohol, heating the product with slightly alkaline water, and distilling in a current of steam. It is a dense, colourless liquid, with a faint, unpleasant odour.

Dibromocymene is prepared by heating bromothymol (100 parts) with phosphoric bromide (46 parts) on a sand-bath until no more hydrogen bromide comes off, and distilling the product in a current of steam. It is a heavy, colourless oil, boiling at 272°. When heated in a sealed tube with nitric acid of sp. gr. 1·12 for 36 hours at 180°, it is converted into dibromoterephthalic acid, which melts at 316—317° to a brown liquid. The ethyl salt of this acid melts at 123—125°. These reactions indicate that the product obtained is paradibromocymene. Consequently the constitution of bromothymol must be

$$[Me : OH : Pr : Br = 1 : 3 : 4 : 6].$$

Nitrobromothymol,

$$C_6HBrMePr(NO_2){\cdot}OH\ [Me : OH : Pr : Br = 1 : 3 : 4 : 6]$$

(compare Abstr., 1886, 1016), prepared by the action of fuming nitric acid (sp. gr. 1·46) on a solution of bromothymol in glacial acetic acid, forms thick, yellow prisms which melt at 106—107°. It separates from its solution in hot light petroleum in slender, prismatic needles which melt at 107—108°. The mother liquor from

the nitrobromothymol, on further evaporation, gave a reddish-brown oil, supposed to be an isomeride, and now under investigation.

S. B. A. A.

Isomerism of Halogenthymoquinones. By F. KEHRMANN (*Ber.*, 22, 3263—3270; compare Abstr., 1889, 1184).—Mazzara (*Gazzetta*, 19, 337) has stated that the bromothymoquinone obtained from bromonitrothymol is identical with the compound obtained from bromonitrocarvacrol, and also that dinitrothymol and dinitrocarvacrol yield one and the same hydroxythymoquinone; the author's experiments, however, seem to show that Mazzara's conclusions are erroneous.

Bromothymoquinone [O_2 : Me : Br : Pr = 1 : 4 : 2 : 3 : 5] is formed by oxidising dibromothymol [OH : Pr : Br_2 : Me = 1 : 2 : 4 : 6 : 5] with chromic acid, by oxidising bromamidothymol [OH : Pr : NH_2 : Me : Br = 1 : 2 : 4 : 5 : 6] with ferric chloride and by oxidising bromothymolparasulphonic acid [OH : Pr : SO_3H : Me : Br = 1 : 2 : 4 : 5 : 6] with chromic acid. It can be easily prepared in large quantities by dissolving thymol (1 mol.) in glacial acetic acid and gradually adding a glacial acetic acid solution of bromine (2 mols.) to the well-cooled solution. Water is added, the precipitated oil separated, dissolved in a little glacial acetic acid, and treated with a glacial acetic acid solution of chromic acid in the cold until no further development of heat occurs. The product is then precipitated with water, distilled with steam, and crystallised from cold ether. It forms long, hexagonal, orange prisms melting at 47—48°. This compound is identical with the bromoquinone obtained by Mazzara and Discalzo (Abstr., 1886, 1019) by oxidising orthobromoparamidothymol with nitrous acid and also with the β-bromothymoquinone prepared by Schniter (Abstr., 1887, 720) by treating thymoquinone with hydrobromic acid and oxidising the product with ferric chloride. The *oxime*, $C_{10}H_{12}BrNO_2$ [NOH : Me = 1 : 2], crystallises in long, lemon-yellow needles, melts at 148—152°, and is readily soluble in alcohol, glacial acetic acid, benzene, and ether, but only sparingly in hot, and insoluble in cold water. When warmed for a short time with nitric acid of sp. gr. 1·42 it is converted into dinitrothymol melting at 54—55°. The *sodium*-derivative crystallises in small, violet-brown needles, and is readily soluble in water, but only sparingly in concentrated alkalis. The *potassium*-derivative crystallises in greenish-brown needles, the ammonium-derivative in small, reddish-brown prisms. The *acetyl*-derivative, $C_{12}H_{14}BrNO_3$, separates from dilute alcohol in yellow crystals, melts at 83°, and is readily soluble in all organic solvents. When the oxime is treated with stannous chloride and alcoholic solution of hydrogen chloride, it is converted into a bromamidothymol identical with the compound prepared by Mazzara and Discalzo (*loc. cit.*) by reducing orthobromoparanitrothymol, and also with the substance obtained by Andresen (Abstr., 1881, 590) by treating thymoquinonechlorimide with hydrobromic acid.

Bromothymoquinone [O_2 : Me : Pr : Br = 1 : 4 : 2 : 5 : 6] can be obtained by oxidising bromocarvacrolparasulphonic acid

[OH : Me : SO_3H : Pr : Br = 1 : 2 : 4 : 5 : 6]

or bromamidocarvacrol [OH : Me : NH_2 : Pr : Br = 1 : 2 : 4 : 5 : 6] with chromic acid. It crystallises from alcohol in large, orange plates, melts at 54—55°, sublimes readily, and is volatile with steam. It is readily soluble in alcohol, ether, benzene, and glacial acetic acid. The *oxime* [Me : NOH = 2 : 4], prepared by boiling an alcoholic solution of the quinone for four to five days with a large excess of hydroxylamine hydrochloride, crystallises from alcohol in large, lemon-yellow rhombohedra, melts at 148° with decomposition, and is readily soluble in alcohol, ether, &c. It is most probably identical with the bromonitrosocarvacrol prepared by Mazzara (*loc. cit.*) by brominating nitrosocarvacrol. F. S. K.

Action of Aniline on Citraconic Acid and on Itaconic Acid. By R. ANSCHÜTZ, F. REUTER and O. SCHARFENBERG (*Annalen*, **254**, 129—152; compare Abstr., 1888, 594).—Aniline citraconate separates as a jelly when citraconic acid is treated with aniline in dry ethereal solution. It separates from boiling water in crystals and melts at 90°, being converted into mesaconanilic acid (m. p. 153°).

When finely-divided citraconanil (compare Gottlieb, *Annalen*, **77**, 77) is dissolved in warm baryta, it is converted into mesaconanilic acid.

Mesaconanilic acid dissolves unchanged in cold alkaline carbonates, but when heated above its melting point, or when its aqueous solution is boiled, it is converted into citraconanil. Mesaconanilic acid is the principal product of the action of aniline (1 mol.) on citraconic acid (1 mol.) in cold aqueous solution, but small quantities of citraconanil are also formed.

Mesaconanilic acid is most conveniently prepared by treating citraconic anhydride with aniline in well-cooled ethereal or chloroform solution; it is decomposed by boiling hydrochloric acid and by boiling alkalis, yielding mesaconic acid.

The above experiments show that the anilic acid obtained from citraconanil by boiling it with baryta is identical with that prepared from citraconic anhydride and aniline, and also with that obtained from aniline citraconate.

Gottlieb's and Michael and Palmer's (Abstr., 1888, 461) citraconanilic acid (m. p. 175°) is named by the authors mesaconanilic acid because it yields mesaconic acid when treated with potash under conditions which do not change citraconic acid into mesaconic acid.

Itaconanilic acid, $C_{11}H_{11}NO_3$, can be obtained in a pure condition by treating itaconic acid with aniline in well-cooled ethereal solution. It melts at 151·5°, and is readily soluble in alcohol and hot water; it dissolves unchanged in cold sodium carbonate, but when boiled with potash, water, or hydrochloric acid, it is converted into itaconic acid.

The compound prepared by Gottlieb and also by Michael and Palmer (*loc. cit.*), and termed by them itaconanilic acid, does not behave like an anilic acid, and is, therefore, named *pseudoitaconanilic* acid by the authors. It can be obtained in the following manner:—Ethyl itabromopyrotartrate is heated at 100° with aniline (2 mols.) for four to five hours, the alcoholic solution separated from the

crystals of aniline hydrobromide, and washed with water; the residual brown oil is dissolved in ether, the solution dried, and the ether evaporated at a low temperature. The crude product (ethyl itanilidopyrotartrate) is boiled with alcoholic potash and the solution acidified; on evaporating, crystals of pseudoitaconanilic acid (m. p. 190°) separate from the solution. This synthesis of pseudoitaconanilic acid seems to show that it is an anilidoparaconic acid,

$$\begin{matrix} NPh\cdot CH_2 \\ | \\ CO-CH_2 \end{matrix}>CH\cdot COOH,$$

as does also its behaviour with phosphoric chloride.

Pseudoitaconanilic chloride, $\begin{matrix} NPh\cdot CH_2 \\ | \\ CO-CH_2 \end{matrix}>CH\cdot COCl$, is obtained when the acid is suspended in chloroform and treated with phosphoric chloride at 50°; it is a yellow, crystalline substance, and is very readily reconverted into the acid by water.

Pseudoitaconanilic acid anilide, $\begin{matrix} NPh\cdot CH_2 \\ | \\ CO-CH_2 \end{matrix}>CH\cdot CONPh$, is easily obtained by treating the preceding compound with aniline in chloroform solution; it is identical with Gottlieb's itaconic acid anilide, and, when heated with concentrated hydrochloric acid, it is reconverted into pseudoitaconanilic acid.

Pseudoitaconanilic acid is decomposed by boiling baryta-water, yielding the barium salt of β-anilidopyrotartrate, but it is not acted on by potash at 100° or by boiling hydrochloric acid; when barium β-anilidopyrotartrate is treated with hydrochloric acid, it yields pseudoitaconanilic acid.

Pseudoitaconparatolilic acid, $\begin{matrix} C_6H_4Me\cdot N-CH_2 \\ | \\ CO\cdot CH_2 \end{matrix}>CH\cdot COOH$, prepared by heating itaconic acid with paratoluidine in aqueous solution, crystallises from boiling water in slender, colourless needles, and melts at 184—185°. It is readily soluble in hot alcohol and chloroform, but only sparingly in cold alcohol, and insoluble in ether.

Pseudoitaconphenylhydrazilic acid, $\begin{matrix} NHPh\cdot N-CH_2 \\ | \\ CO\cdot CH_2 \end{matrix}>CH\cdot COOH$, prepared in like manner, crystallises from hot water or alcohol in small, yellow prisms, melts at 193—194°, and is only sparingly soluble in ether and chloroform.

Pseudoitacon-α-naphthilic acid, $\begin{matrix} C_{10}H_7\cdot N-CH \\ | \\ CO\cdot CH_2 \end{matrix}>CH\cdot COOH$, separates from hot water as a colourless, crystalline powder, melts at 205—206°, and is only very sparingly soluble in ether and chloroform.

F. S. K.

Dihydroxydiphenylamine and a Brownish-red Colouring Matter. By SEYEWITZ (*Compt. rend.*, **109**, 946—949).—*Dihydroxydiphenylamine*, $NH(C_6H_4\cdot OH)_2$, obtained by heating resorcinol in sealed tubes at 190—200° for 10 hours with four times its weight of ammoniacal calcium chloride, may be purified by repeated solution in alcohol and precipitation by water, and is finally crystallised from hot

aqueous alcohol. It forms brownish-yellow, indistinct, microscopic crystals, only slightly soluble in cold or hot water, insoluble in benzene or ether, but very soluble in alcohol, yielding a solution with a fluorescence similar to that of fluoresceïn. It is somewhat soluble in hydrochloric acid, but yields no crystallisable hydrochloride, is soluble with a green colour in concentrated sulphuric acid, and is coloured violet by nitric acid. It dissolves readily in alkalis, and with barium hydroxide forms an unstable compound which crystallises from alcohol in very distinct yellow plates. With sodium nitrite in acid solution, it yields a violet-red nitroso-derivative, and it forms colouring matters with diazo-derivatives. If distilled with zinc-powder, it yields diphenylamine.

If resorcinol and ammoniacal calcium chloride in the same proportions are heated at 300° for about eight hours, a brownish-red colouring matter is formed, and is left undissolved when the product is treated with water. This colouring matter contains nitrogen, and has many of the properties of the amines. It dissolves in hydrochloric acid, and is precipitated by ammonia; it melts at 70—72°, is insoluble in water and alkalis, but dissolves readily in alcohol; it yields a diazo-derivative which forms colouring matters with phenols.

It gives fine brown colours on cotton mordanted with tannin and tartar emetic, or on linen mordanted with potassium dichromate.

C. H. B.

Benzoyl-derivatives. By O. HINSBERG and L. v. UDRÁNSZKY (*Annalen*, **254**, 252—258).—Monohydroxy- and amido-compounds can be easily converted into the corresponding benzoyl-derivative by Baumann's method (Abstr., 1887, 228); methylaniline yields a benzoyl-derivative less easily. The benzoyl-derivative of metanitraniline can be easily obtained, but not so those of ortho- and paranitraniline. Orthonitrophenol does not yield a benzoyl-derivative when it is treated by Baumann's method, but the para-compound does so fairly readily. The dihydroxybenzenes are easily converted into the dibenzoyl-derivatives.

Dibenzoylorthophenylenediamine, $C_{20}H_{16}N_2O_2$, crystallises in plates and melts above 280°. The corresponding *para*-compound crystallises in colourless plates, melts above 300°, and is only sparingly soluble in glacial acetic acid, alcohol, and ether, and almost insoluble in water; it yields a *nitro*-derivative, $NO_2 \cdot C_6H_3(NHBz)_2$, which crystallises in small, yellow needles, melts at 251°, and is converted into nitroparaphenylenediamine (m. p. 137°) by sulphuric acid.

Dibenzoylorthotoluylenediamine melts at 263—264°, and not at 260—261° as stated by Hübner (*Annalen*, **208**, 314); when boiled for a short time with concentrated hydrochloric acid, it is converted into benzoyltoluylenediamine, but when boiled with concentrated sulphuric acid for some hours, it is converted into toluylenediamine.

Dibenzoyl-α-β-naphthylenediamine, $C_{10}H_6(NH \cdot COPh)_2$, crystallises in reddish plates, melts at 291°, and is only sparingly soluble in alcohol and glacial acetic acid, and almost insoluble in water.

Tribenzoyltriamidobenzene [1 : 3 : 4] crystallises from glacial acetic acid in small, colourless needles, melts at 260°, and is sparingly soluble in the ordinary solvents.

Dibenzoylorthamidophenol and the corresponding para-compound can be easily obtained by Baumann's method.

Tetrabenzoyltriamidophenol [OBz : $(NHBz)_3$ = 1 : 2 : 4 : 6] crystallises from hot glacial acetic acid in slender, colourless needles, melts at 256°, and is almost insoluble in alcohol and water. It is not acted on by strong mineral acids or by a mixture of potassium dichromate and sulphuric acid, but when heated with strong nitric acid, it yields a yellowish compound—probably a nitro-derivative.

F. S. K.

Formation of Amidines. By A. KUHLWEIN (*Chem. Centr.*, 1889, ii, 917).—When carbotriphenyltriamine is heated with carbon bisulphide at 150°, a yellow substance is formed which cannot be obtained in crystals; it is probably amidobenzothioanilide. Cyanogen forms a readily decomposable substance with carbotriphenyltriamine.

Amidotoluylenediorthotolylamidine, $C_{22}H_{23}N_3$, melting at 155°, and the isomeric para-compound, melting at 149·5—150°, are prepared from the respective toluidines by warming with carbon tetrachloride. The hydrochloride and nitrate of the former are sparingly soluble; the hydrochloride, nitrate, acetate, sulphate, and oxalate of the latter are readily soluble.

α- and β-naphthylamines also react with carbon tetrachloride; diphenylamine does not appear to do so. J. W. L.

Action of Aromatic Amines on Bromopropiolic Acid and on Substituted Acrylic Acids. By C. F. MABERY and A. H. KRAUSE (*Ber.*, **22**, 3305—3310).—Ethenyldiphenylamidine, $C_{14}H_{14}N_2$ (m. p. 131—132°), is formed, together with a compound melting at 220°, when bromopropiolic acid is treated with aniline in alcoholic solution. The hydrochloride crystallises in needles and melts at 214—215°, the platinochloride in small, yellow prisms. When the base is heated with water at 150° for two hours, it is completely converted into a crystalline compound which melts at 111—112°, and is soluble in water (compare Hofmann, *Ber.*, **2**, 649); at higher temperatures, acetic acid and a compound which is insoluble in acids and in water are formed. The compound melting at 220°, referred to above, is insoluble in hydrochloric acid and almost insoluble in water; it has the composition $C_{15}H_{14}N_2O_2$.

Ethenylditolylamidine, $C_{16}H_{18}N_2$, and a compound melting at 241—242° are obtained when paratoluidine is treated with bromopropiolic acid; the hydrochloride, $C_{16}H_{18}N_2,HCl$, melts at 198—200°. When the base is heated with water at 150°, it is completely converted into a colourless, crystalline compound melting at 145—146°; at higher temperatures it behaves like the corresponding phenyl-compound. The substance melting at 241—242° (see above) has the composition $C_{16}H_{17}N_2O_2$(?), and is insoluble in water and acids.

The compound $C_{17}H_{19}N_2O_2$, prepared by treating bromopropiolic acid with orthotoluidine, crystallises from alcohol in colourless needles, melts at 184—185°, and is insoluble in water and acids, and only sparingly soluble in alcohol.

Metatoluidine combines with bromopropiolic acid with evolution

of carbonic anhydride, yielding a compound which crystallises yellow needles.

α-Naphthylamine (2 mols.) combines with bromopropiolic ac (1 mol.) with evolution of hydrogen bromide, yielding a yello crystalline compound.

A compound of the composition $C_{15}H_{13}N_2Br$ separates in yell crystals when αβ-dibromacrylic acid is treated with aniline in the co It crystallises from alcohol in yellow needles, melts at 145°, and insoluble in water, and only sparingly soluble in acids.

The condensation-product obtained from paratoluidine in li manner crystallises in yellow needles, melts at 165—166°, and has t composition $C_{17}H_{16}N_2Br$; it is almost insoluble in water and aci but soluble in soda. A compound of the composition $C_{17}H_{17}N_2B$ which melts at 164° and is insoluble in soda, is also formed in t reaction.

Orthotoluidine combines with αβ-dibromacrylic acid in alcoho solution, yielding a base of the composition $C_{17}H_{18}N_2Br$; this crystallis from alcohol in pale-yellow needles melting at 115°. The *hydrobromi* $C_{17}H_{18}N_2Br,HBr$, crystallises in yellow needles and melts at 208—20

ββ-Dibromacrylic acid also gives condensation-products with a matic amines. F. S. K.

Action of Potassium Phthalimide on Halogen-compoun containing Oxygen. By C. Schmidt (*Ber.*, **22**, 3249—3257; co pare Goedeckemeyer, Abstr., 1888, 1294).—*Metanitrophenacylphth imide*, $NO_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot N{:}C_8H_4O_2$, is obtained when metanitroph acyl bromide (1 mol.) is mixed with potassium phthalimide (1 mo and the mixture heated at about 100° for an hour. It separates fr hot glacial acetic acid in small, pointed crystals, melts at 204°, and only sparingly soluble in alcohol and cold, glacial acetic acid. It not decomposed by hydrochloric acid or by boiling potash.

Phthalimidopropiophenone, $COPh\cdot C_2H_4\cdot N{:}C_8H_4O_2$, can be obtain by heating a mixture of bromopropiophenone and potassium phth imide at 160—170° for a short time. It crystallises from alcohol large prisms, melts at 85°, and is readily soluble in hot ether, b insoluble in water. The corresponding *acid*, $C_{17}H_{15}NO_4$, prepared treat ng the imido-compound with alcoholic or aqueous potash, cr tallises in slender needles melting at 140°. It dissolves in warm alcoh being thereby partially reconverted into the imide; the same chan takes place when the acid is heated at 100° for two days, but resino products are also formed. The *silver* salt, $C_{17}H_{14}NO_4Ag$, which cryst lises with 1 mol. H_2O, is soluble in water and alcohol, and is read decomposed when heated, yielding a sublimate of phthalimide. aqueous solutions of the ammonium salt, lead salts produce a colo less, ferric salts a brown, and copper sulphate a light-blue precipit which is sparingly soluble in cold water.

Amidopropiophenone hydrochloride, $COPh\cdot C_2H_4\cdot NH_2,HCl$, is form together with resinous products, when propiophenonephthalamic a is boiled for an hour with concentrated hydrochloric acid. The co solution is filtered to separate the phthalic acid, evaporated to dryne the residue taken up with alcohol, and the salt obtained in a crystalli

condition by mixing the filtered solution with ether. The *platinochloride*, $(C_9H_{11}NO)_2,H_2PtCl_6$, forms orange-red crystals. The *picrate*, $C_9H_{11}NO,C_6H_3N_3O_7$, crystallises in yellow needles, turns brown at 140°, melts and turns black at 160°, and decomposes completely at 170°. When the base is set free by treating one of the salts with potash, it seems to decompose very quickly yielding resinous products; it gives the carbylamine reaction. On the addition of ammonia to a solution of the hydrochloride there is produced after some time a yellow precipitate, which dissolves in hydrochloric acid yielding a red solution. When the ammoniacal solution is extracted with ether, two compounds are obtained; the one is a colourless, crystalline substance melting at 124°, the other a volatile liquid with an aromatic odour recalling that of benzaldehyde.

When an alcoholic ammoniacal solution of bromopropiophenone, prepared from propionic chloride, benzene, and aluminium chloride by Claus and Wollner's method (Abstr., 1885, 1136), is kept for a long time and then allowed to evaporate, a colourless, crystalline substance melting at 124° separates from the solution. This compound is most probably identical with the crystalline product obtained by decomposing amidopropiophenone hydrochloride with ammonia, and is probably dimethyldiphenylaldine. It is a feeble base, and dissolves in concentrated hydrochloric acid, but is reprecipitated on adding water; in a warm solution of the hydrochloride, platinic chloride produces an orange precipitate which seems to have the composition $C_4N_2Ph_2Me_2,H_2PtCl_6$, and is decomposed by water.

Diphenylaldine platinochloride, $C_4N_2H_2Ph_2,H_2PtCl_6$, prepared by adding a solution of platinic chloride in fuming hydrochloric acid to a warm solution of isoindole (diphenylpyrazine) in fuming hydrochloric acid, crystallises in small, bronze-coloured plates, and does not melt below 300°; it is quickly and completely decomposed by water, alcohol, and dilute hydrochloric acid, with separation of the base.

Phenoxyethylphthalimide, $OPh{\cdot}C_2H_4{\cdot}N{:}C_8H_4O_2$, is formed when potassium phthalimide is heated at 190—200° for two hours with bromethyl phenyl ether (β-bromophenetoïl). It crystallises in plates, melts at 129—130°, and is soluble in boiling alcohol, benzene, and carbon bisulphide. *Phenoxyethylphthalamic acid*, $C_{16}H_{15}NO_4$, prepared by warming the imide with potash, is a crystalline compound melting at 125°; it is reconverted into the imide when heated at 140°, when boiled with alcohol, or when hydrogen chloride is passed into its alcoholic solution.

Phenoxyethylamine hydrochloride, $OPh{\cdot}C_2H_4{\cdot}NH_2,HCl$, is obtained by heating the preceding compound with concentrated hydrochloric acid, and separating the phthalic acid and the regenerated imide by filtration. It crystallises from alcohol in long, flat needles, and melts at 215°. The *platinochloride*, $(C_8H_{11}NO)_2,H_2PtCl_6$, crystallises in small, golden needles. The *picrate*, $C_8H_{11}NO,C_6H_3N_3O_7$, forms small, light-yellow, granular crystals. The free base separates as a colourless oil when the hydrochloride is decomposed with potash; it is soluble in ether, and absorbs carbonic anhydride with great readiness forming a crystalline carbonate.

Picryl chloride and potassium phthalimide react very readily when warmed together at about 70°, yielding *picrylphthalimide*, $C_6H_2(NO_2)_3N:C_8H_4O_2$. This compound separates from glacial acetic acid in large, yellow crystals, melts at 259°, and dissolves in boiling soda with a brownish-red coloration; it is decomposed by concentrated hydrochloric acid at 180° yielding phthalic acid and picramide (m. p. 188°). F. S. K.

Substitution of the Anilido-group for a Halogen-atom in the Benzene-nucleus. By M. SCHÖPFF (*Ber.*, **22**, 3281—3289; compare Abstr., 1889, 772).—*Metanitroparanilidobenzoic acid* (*metanitrodiphenylamineparacarboxylic acid*) [COOH : NO_2 : NHPh = 1 : 3 : 4] is formed when parabromometanitrobenzoic acid is boiled with excess of aniline; the yield is almost quantitative. It crystallises from alcohol in garnet-red needles, melts at 254°, and is readily soluble in alcohol, acetone, chloroform, and amyl alcohol, but only moderately easily in benzene, and insoluble in light petroleum. The *sodium* salt, $C_{13}H_9NO_4Na$, crystallises from alcohol in small, red, anhydrous plates and from dilute alcohol in orange needles containing 1 mol. H_2O, which is expelled at 100°. The *barium* salt, $(C_{13}H_9NO_4)_2Ba + 3H_2O$, crystallises in small, orange needles. The other metallic salts are yellow or orange, and are only sparingly soluble. The *ethyl* salt, $C_{15}H_{14}N_2O_4$, separates from alcohol in hexagonal crystals, melts at 123°, and is readily soluble in acetone, chloroform, and benzene, but only sparingly in ether, and almost insoluble in light petroleum.

Metamidoparanilidobenzoic acid [COOH : NH_2 : NHPh = 1 : 3 : 4], prepared by reducing the nitro-acid with an alcoholic solution of ammonium sulphide at 120°, crystallises from water in small, colourless needles, melts at 153°, and turns reddish on exposure to the air. It is readily soluble in alcohol, acetone, and chloroform, but only moderately easily in benzene, and is insoluble in light petroleum; it dissolves in concentrated sulphuric acid with a reddish coloration, which becomes dark red on adding a trace of nitric acid. The *hydrochloride*, $C_{13}H_{12}N_2O_2,HCl$, crystallises in needles, and is decomposed by water. The *ethyl* salt, $C_{15}H_{16}N_2O_2$, prepared by reducing the ethyl salt of the nitro-acid with alcoholic ammonium sulphide, crystallises from dilute alcohol in colourless plates, and melts at 76—77°. When the acid is distilled, it is converted into orthamidodiphenylamine (phenylorthophenylenediamine) identical with the compound obtained by reducing orthonitrodiphenylamine (*loc. cit.*) with ammonium sulphide in alcoholic solution.

Phenylazimidobenzoic acid, $N{<}{\overset{NPh}{\underset{N}{}}}{>}C_6H_3{\cdot}COOH$, is obtained when metamidoparanilidobenzoic acid is treated with sodium nitrite in dilute hydrochloric acid solution or, better, with amyl nitrite and hydrochloric acid in alcoholic solution. It crystallises from alcohol in rose-coloured needles melting at 272°.

Metanitroparatoluilidobenzoic acid [COOH : NO_2 : $NH{\cdot}C_6H_4Me$ = 1 : 3 : 4], prepared by heating bromonitrobenzoic acid with paratoluidine, is a crystalline compound melting at 257°; it resembles the corresponding anilido-derivative in its behaviour.

Metanitroparahydroxyanilidobenzoic acid [$COOH : NO_2 : NH{\cdot}C_6H_4{\cdot}OH = 1 : 3 : 4$], prepared by heating amidophenol with an alcoholic solution of bromonitrobenzoic acid at 120° for seven hours, crystallises in small brown needles, melts at 260—261°, and is readily soluble in alcohol and acetone, but only sparingly in benzene, chloroform, light petroleum, and hot water. F. S. K.

Synthesis of Hydratropic Acid. By V. OLIVERI (*Gazzetta*, **18**, 572—575).—Pure benzyl cyanide (18 grams) is gradually added to a solution of sodium (3·5 grams) in anhydrous methyl alcohol (60 c.c.), methyl iodide (40 grams) is then added, and the mixture heated on the water-bath in a reflux apparatus until a test portion diluted with water no longer reddens blue litmus; the alcohol and excess of methyl iodide are then distilled off, and the oily residue washed, dried, and distilled. The distillate, which consists of a mixture of the nitriles of hydratropic and phenylacetic acids, is saponified, decomposed with dilute sulphuric acid, dried, and distilled. A mixture of hydratropic acid and phenylacetic acid passes over at 260—263°, and from this the former may be isolated by strongly cooling, filtering off the crystalline deposit which separates, and redistilling the liquid filtrate in a current of steam; the hydratropic acid, $CHMePh{\cdot}COOH$, which passes over is a colourless oil boiling between 260° and 261°.

The author considers that Trinius' synthesis of phloretic acid from paramidohydratropic acid by the diazo-reaction (Abstr., 1885, 529) is open to objection on account of the energetic reagents employed, and proposes to synthesise phloretic acid from parahydroxyphenylacetonitril. S. B. A. A.

Orthocresolglycollic Acid. By A. OGLIALORO and G. CANNONE (*Gazzetta*, **18**, 511).—The acid was prepared by the action of monochloracetic acid on orthocresol, following the directions given by Giacosa for the preparation of phenolglycollic acid. It is somewhat soluble in hot water, less so in cold, crystallising from the hot aqueous solution in nacreous laminæ which melt at 151—152°.

The *sodium salt* (unlike the paracresolglycollate) is very soluble in water. The *barium salt*, $Ba(C_9H_9O_3)_2 + 4H_2O$, is deposited in groups of white laminæ on treating the acid with baryta-water and concentrating the solution; it melts in its water of crystallisation at 120°. The *lead salt*, $Pb(C_9H_9O_3)_2 + H_2O$, is prepared by double decomposition from the barium salt. It is only sparingly soluble in boiling water, and crystallises in small, white prisms. It is easily decomposed. S. B. A. A.

Derivatives of Benzallevulinic Acid. By H. ERDMANN (*Annalen*, **254**, 182—222).—Benzallevulinic acid (γ-phenyl-β-acetylisocrotonic acid), $CHPh{:}CAc{\cdot}CH_2{\cdot}COOH$ (compare Abstr., 1886, 241), melts at 125°. The alkaline salts are very readily soluble in alcohol and water. The *calcium* salt, $(C_{12}H_{11}O_3)_2Ca + 3\frac{1}{2}H_2O$, and the *barium* salt (with $5H_2O$) crystallise in needles, and are very readily soluble in water. The *silver* salt separates unchanged from boiling water. Several other metallic salts were prepared. The *methyl* salt, $C_{13}H_{14}O_3$,

prepared by warming the acid with methyl alcohol and a little concentrated sulphuric acid, is a colourless oil boiling at 200—230° (38 mm.); it combines readily with bromine in chloroform solution yielding an oily product.

Bromobenzyllevulinic acid, $CH_2Ph\cdot CBrAc\cdot CH_2\cdot COOH$, was obtained, but only in an impure condition, by warming finely divided benzallevulinic acid with fuming hydrobromic acid. It melts at 125—130°, and dissolves freely in cold sodium carbonate, but the solution gradually undergoes decomposition.

When benzallevulinic acid is heated at 120° with acetic anhydride and sodium acetate, it yields a yellow, amorphous compound; with acetic chloride in the cold, it gives resinous products, and when treated with fuming nitric acid it seems to yield a mixture of an ortho- and a paranitro-compound.

Aceto-α-naphthol (Abstr., 1888, 488) crystallises from dilute acetic acid in long, yellowish-brown needles, melts at 168°, and is readily soluble in alcohol and glacial acetic acid, but only sparingly in most of the other ordinary solvents, and very sparingly in water. The sodium-derivative crystallises in yellow plates; its aqueous solution gives the α-naphthol reaction with paradiazonaphthalenesulphonic acid, an intense blue coloration with quinone chlorimides, and with silver nitrate a colourless precipitate, which rapidly darkens on warming. The *acetyl*-derivative, $C_{14}H_{12}O_3$, crystallises in colourless needles, melts at 108—109°, and is insoluble in cold alkalis. The *oxime*, $C_{12}H_{11}O_2N$, prepared by boiling the ketone with hydroxylamine in alkaline solution, crystallises in colourless, microscopic prisms, melts at 173—174°, and is soluble in alcohol and toluene.

Benzyllevulinic acid, $CH_2Ph\cdot CHAc\cdot CH_2\cdot COOH$, is obtained when benzallevulinic acid is suspended in hot water and treated with excess of 8 per cent. sodium amalgam, the solution being kept acid in order to avoid the formation of benzylvalerolactone (see below). The yield is 95 per cent. of the theoretical quantity. It crystallises from dilute alcohol in long, compact needles, melts at 98—99°, and boils at 230—235° (40 mm.) with slight decomposition. It dissolves in concentrated sulphuric acid yielding a yellow solution, which turns green, and then greenish-blue if kept for two or three days. The *calcium* salt $(C_{12}H_{13}O_3)_2Ca + 3H_2O$, crystallises in needles which effloresce on exposure to the air. The *silver* salt crystallises unchanged from hot water, but it gradually darkens on exposure to light. The *oxime*, $C_{12}H_{15}O_3N$, is a mobile oil readily soluble in alkalis and in mineral acids, but only sparingly in water.

Benzylangelicalactone, $C_{12}H_{12}O_2$, prepared by heating benzyllevulinic acid at its boiling point for 10—20 minutes, is a yellowish oil sparingly soluble in boiling water. It is only very slowly decomposed by boiling water, but it is reconverted into benzyllevulinic acid by boiling baryta-water. It combines with bromine in carbon bisulphide solution, yielding an oily additive compound.

Benzylvalerolactone, $C_{12}H_{14}O_2$, is obtained when benzal- or benzyllevulinic acid is reduced with sodium amalgam in alkaline solution. It separates from carbon bisulphide in well-defined crystals, melts at 86°, and is very readily soluble in toluene, but only sparingly in hot

water; it is not changed by cold alkaline carbonates, but is converted into benzylhydroxyvaleric acid when heated with alkalis.

β-Benzyl-γ-hydroxyvaleric acid, $OH\cdot CHMe\cdot CH(C_7H_7)\cdot CH_2\cdot COOH$, crystallises from water with 1 mol. H_2O in small prisms, which melt at 55—56°, and lose their water over sulphuric acid; the anhydrous compound melts at 75—76°. It is moderately easily soluble in water, and when boiled with dilute mineral acids is reconverted into the lactone. The *barium* salt crystallises in colourless plates or prisms, and is sparingly soluble in water. The *calcium* salt,

$$(C_{12}H_{15}O_3)_2Ca + 6H_2O,$$

separates from cold water in microscopic prisms.

Phenylangelic-lactone, $C_{11}H_{10}O_2$, prepared by distilling α-phenyl-levulinic acid (Weltner, Abstr., 1884, 747) under reduced pressure (38 mm.), crystallises from a mixture of carbon bisulphide and light petroleum in colourless plates melting at 53°. It is very readily soluble in carbon bisulphide, but only sparingly in light petroleum. It is not decomposed by boiling water, but it is readily converted into the acid by boiling lime-water. When treated with bromine in chloroform solution, it yields an oily additive-compound. F. S. K.

Action of Ethyl Sodiomalonate on Tribromodinitrobenzene. By C. L. JACKSON and W. S. ROBINSON (*Amer. Chem. J.*, 11, 541—557). —A continuation of the research described in a previous paper (Abstr., 1889, 781). The formation of ethyl bromodinitrophenyl-malonate by the action of ethyl sodiomalonate on tribromodinitrobenzene is shown to take place according to the following equations:—

$$(1.)\ C_6HBr_3(NO_2)_2 + CHNa(COOEt)_2 = NaBr + C_6HBr_2(NO_2)_2\cdot CH(COOEt)_2.$$

$$(2.)\ C_6HBr_2(NO_2)_2\cdot CH(COOEt)_2 + CHNa(COOEt)_2 = C_6HBr_2(NO_2)_2\cdot CNa(COOEt)_2 + CH_2(COOEt)_2.$$

$$(3.)\ = C_6H_2Br(NO_2)_2\cdot CNa(COOEt)_2 + CHBr(COOEt)_2.$$

$$(4.)\ CHNa(COOEt)_2 + H_2O = NaOH + CH_2(COOEt)_2.$$

$$(5.)\ CHBr(COOEt)_2 + NaOH = NaBr + CH(OH)(COOEt)_2.$$

Of these reactions 1, 2, and 3 take place before, 4 and 5 after the addition of water used in working up the product.

Ethyl bromodinitrophenylmalonate, $C_6H_2Br(NO_2)_2\cdot CH(COOEt)_2$ [= 3 : 4 : 6 : 1], was prepared by making a strong solution of 20 grams of tribromodinitrobenzene, $C_6HBr_3(NO_2)_2$ [= 1 : 3 : 5 : 4 : 6], in benzene, and treating it with ethyl sodiomalonate, made by adding to 16 grams of ethyl malonate the sodium ethoxide obtained from 2·3 grams of sodium and 100 to 125 c.c. of alcohol. The mixture was allowed to remain all night at the ordinary temperature, and was then treated with water, and the aqueous solution separated by means of a separating funnel from the benzene solution, which contained unaltered tribromodinitrobenzene, together with an oily product of the reaction. The ethyl bromodinitrophenylmalonate was thrown down from the aqueous solution as a yellowish precipitate by adding

dilute sulphuric acid; when recrystallised from hot alcohol, it melted at 76°. The yield was only half the theoretical, much remaining dissolved in the oily product of the reaction. It was shown that two-thirds of the bromine contained in the original tribromodinitrobenzene is removed as sodium bromide, and also that the oily product of the reaction gives tartronic acid when heated with strong hydrochloric acid in a sealed tube at 130°; hence the reaction is represented by the equations given above.

Metabromodinitrophenylacetic acid, $C_6H_2Br(NO_2)_2\cdot CH_2\cdot COOH$ [= 3 : 4 : 6 : 1], was prepared by boiling 2 grams of ethyl bromodinitrophenylmalonate with 100 c.c. of dilute sulphuric acid (of sp. gr. 1·44) in a reflux apparatus until it all dissolved. The solution, on cooling, deposited the acid in long, pale-yellow needles, which may be recrystallised from water containing a few drops of sulphuric acid, but are decomposed by pure water and by alcohol. The yield is quantitative.

Metabromodinitrophenylacetic acid melts at 177°, and dissolves in acetone, glacial acetic acid, and ether, but not to any extent in the other common solvents. When boiled with alcohol or water, it is decomposed, losing carbonic anhydride, and forming a bromodinitrotoluene which has been shown to have the constitution

$$[CH_3 : Br : (NO_2)_2 = 1 : 3 : 4 : 6].$$

From this follow the formulæ which have been assigned to the compounds mentioned above. The acid dissolves in ammonia, giving a solution which is colourless if the acid is in excess, green if the ammonia is in slight excess, brown if it is in large excess. The colourless solution gives precipitates with salts of many of the heavy metals. The precipitate with silver nitrate is at first flocculent, but becomes crystalline after a time; it has the formula

$$C_6H_2Br(NO_2)_2\cdot CH_2\cdot COOAg + H_2O.$$

With aqueous soda, the acid gives a green coloration, changing to brown as excess of soda is added. With acids, the green solution gives a colourless precipitate, which becomes purple when moistened with alcohol. The brown solution on treatment with acids yields a viscous red substance, probably of the nature of a phenol. In both these reactions bromine is removed. C. F. B.

Action of Aniline on Ethyl Oxalacetate and Ethyl Methyloxalacetate. By W. Wislicenus and K. Spiro (*Ber.*, **22**, 3348—3352).—When aniline and ethyl oxalacetate are mixed in the cold, water separates, and *ethyl aniloxalacetate*,

$$COOEt\cdot C(NHPh)\colon CH\cdot COOEt,$$

is formed. This is a yellowish oil, which under a pressure of 10 mm. of mercury begins to distil at 200°, but at the same time undergoes considerable decomposition. It is insoluble in water and dilute acids or alkalis, easily soluble in alcohol and ether. Alkalis and acids cause a separation of aniline. When heated, water and alcohol separate, and two substances, $C_{11}H_{15}NO_3$, melting at 107—108°, and $C_{12}H_{11}NO_3$,

melting at 212—213°, are formed, but have not been further investigated. When the action of aniline on ethyl oxalacetate is carried on at a high temperature (about 130—150° is found to be the best), 2 mols. of aniline enter into the reaction, phenylamidomaleïc acid phenylimide (Michael, Abstr., 1886, 698) being formed.

Aniline acts less readily on ethyl methyloxalacetate, but, on warming, *ethyl anilomethyloxalacetate* is formed. When, however, the ethyl salt is heated with aniline (2 mols.) at about 180°, *methylanilidomaleïc acid phenylimide*, $NPh{:}C<\begin{matrix}CO\text{—}NPh\\ CHMe\cdot CO\end{matrix}$, is formed. It is easily soluble in boiling glacial acetic acid and alcohol, insoluble in water and ether. It crystallises in glistening, golden-yellow scales, and melts at 158—160° to a reddish-yellow liquid. L. T. T.

Sulphone-derivatives. By R. Otto (*J. pr. Chem.* [2], **40**, 505—564).

1. Action of alkaline sulphinates on polyhalogen-derivatives of hydrocarbons, in which the halogen-atoms are linked to one carbon-atom:—

The action of sodium aromatic-sulphinates on methylene iodide has been investigated by Michael and Palmer (Abstr., 1885, 536), and by the author (Abstr., 1888, 482). There is here given the crystallography of methylphenylsulphone, methylene-iodophenylsulphone, methylparatolylsulphone and methylene-iodoparatolylsulphone.

Ethylidenechlorophenylsulphone, $CHMeCl\cdot SO_2Ph$, is obtained when ethylidene chloride (1 mol.) and sodium benzenesulphinate (2 mols.) are heated together in alcohol in a sealed tube at 150—160°. Ethyl chloride escapes on opening the tube; water separates from the contents a dark-brown ethereal solution containing much phenyl bisulphide, little phenylbenzenethiosulphonate and ethylidenechlorophenylsulphone, together with unaltered ethylidene chloride. The aqueous solution contains unaltered sulphinate, sodium chloride, and sodium sulphonate. The sulphone is separated by evaporating the ether, and fractionally crystallising from alcohol; it melts at 52°. It differs from the isomeric phenylsulphonethyl chloride (Abstr., 1885, 263) in that it is not converted into ethylenediphenylsulphone when heated with sodium benzenesulphinate.

When sodium paratoluenesulphinate is substituted for the benzenesulphinate in the above reaction, ethylidenechloroparatolylsulphone (see below) is obtained.

When the above experiments are compared with those on methylene iodide (Abstr., 1888, 482), it is evident that the SO_2R' group is more easily substituted for the halogen in the methylene-derivative than in the ethylidene-derivative.

Benzylidenechlorophenylsulphone, $CHPh{\cdot}Cl{\cdot}SO_2Ph$, is prepared by heating benzylidene chloride (10 grams) with sodium benzenesulphinate (20 grams) in alcohol in a reflux apparatus, the solution being kept neutral by addition of sodium carbonate. The alcohol is distilled off, the residue treated with water, and immediately shaken with ether, which does not dissolve the sulphone. It crystallises from glacial acetic acid in small, broad, vitreous, sparingly soluble

needles (m. p. not given). Benzaldehyde, phenyl benzenethiosulphonate, phenyl mercaptan, and phenyl bisulphide are dissolved by the ether, the sodium chloride and sodium benzenesulphonate by the water.

Benzylidenechloroparatolylsulphone, $CHPhCl\cdot SO_2\cdot C_7H_7$, obtained in like manner from benzylidene chloride and sodium paratoluenesulphinate, crystallises from hot glacial acetic acid in small, yellowish-white, lustrous needles melting at 203°.

The above reactions confirm the author's generalisation as to the action of alkaline sulphinates on dihalogen derivatives of hydrocarbons (Abstr., 1888, 482).

The action of sodium benzenesulphinate on the trihalogen-derivatives of hydrocarbons, chloroform, and methylchloroform, has been described before (Abstr., 1888, 841); that ethylidenedisulphone should be produced in the case of methylchloroform is remarkable, and indicates that one of the chlorine-atoms first displaces a hydrogen-atom in the methyl-group, forming $CH_2Cl\cdot CHCl_2$ (compare the formation of symmetrical succinic acid from ethylidene chloride and potassium cyanide, Erlenmeyer and Simpson, *Zeit. Chem.* 2[?], 3, 593, 673).

Benzylphenylsulphone (Abstr., 1888, 841) crystallises in lustrous, slender prisms melting at 146—147°, and insoluble in water, but soluble in alcohol. Its crystallography is given.

The SO_2R group is more easily substituted for chlorine in benzotrichloride (phenylchloroform) than in methylchloroform, and more easily in this than in chloroform (compare Busz and Kekulé, Abstr., 1888, 302). In trihalogen-derivatives of hydrocarbons in which three atoms of halogen are linked to one carbon-atom, only one such atom is displaced by the SO_2R-group, the others being displaced by hydrogen.

2. Action of alkaline sulphinates on polyhalogen derivatives of fatty acids, in which the halogen-atoms are linked to one carbon-atom:—

When sodium benzenesulphinate (6·5 grams) is heated on the water-bath with dichloracetic acid (2·5 grams) neutralised with sodium hydroxide, *chloromethylphenylsulphone*, identical with methylenechlorophenylsulphone (Abstr., 1888, 483), sodium chloride, and sodium carbonate are formed. *Chloromethyltolylsulphone*, obtained from sodium toluenesulphinate and dichloracetic acid, crystallises in vitreous tables, whose crystallography is given: it melts at 84°, is insoluble in water, but soluble in hot alcohol or benzene. It can also be obtained by the action of methylene chloride on sodium toluenesulphinate.

The action of sodium benzenesulphinate on sodium α-dichloropropionate produces ethylenediphenylsulphone (Abstr., 1885, 261), and may be compared with that of the same salt on methylchloroform (see above). A small quantity of ethylidenechlorophenylsulphone is obtained at the same time. *Diphenylsulphonethylamine*, obtained by the action of ammonia on ethylenediphenylsulphone, has been described before (Abstr., 1885, 537); its crystallography is here given.

Ethylidenechloroparatolylsulphone is the chief product of the action of sodium paratoluenesulphinate on sodium α-dichloropropionate, only

a little ethylidenediparatolylsulphone (Abstr., 1885, 538) being produced. It crystallises in thin, rhombic tables (crystallography given) melting at 84°; it is unchanged by heating with sodium toluenesulphinate. The corresponding bromo-derivative was not obtained when sodium α-dibromopropionate was substituted for the α-dichloropropionate.

Ethyl dichloracetate (1 mol.) was heated with sodium benzenesulphinate and toluenesulphinate, respectively (2 mols.), in alcohol for eight days; chloromethylphenylsulphone and chloromethyltolylsulphone, respectively, were obtained, together with sodium chloride, sodium sulphonate, and, in the former case, sodium phenylsulphonacetate.

There is no action between sodium benzenesulphinate or toluenesulphinate and trichloracetate when heated together.

3. Action of chlorine and bromine on sulphonecarboxylic acids:

Dichloromethylphenylsulphone, $CHCl_2 \cdot SO_2Ph$, is obtained, together with carbonic anhydride, when chlorine is passed through warm aqueous phenylsulphonacetic acid in diffused daylight, as an oil which separates from alcohol or ethyl acetate in prismatic crystals, melting at 59°.

On mixing bromine with phenylsulphonacetic acid (equal mols.), two bromo-derivatives are obtained; these may be separated by crystallising from hot alcohol, when *bromomethylphenylsulphone* remains dissolved; it forms thick, lustrous, tabular crystals melting at 46—48°, and insoluble in water. *Dibromomethylphenylsulphone* forms many-sided crystals (melting point not given), insoluble in water.

There have also been obtained in the same way, *dichloromethylparatolylsulphone*, which forms lustrous crystals melting at 114°; *bromomethylparatolylsulphone*, forming slender needles melting at 90—92°; *dibromomethylparatolylsulphone*, which forms prismatic crystals melting at 116—117°. These are all soluble in hot alcohol, but insoluble in water. The crystallography of the last five compounds is given.

It is thus seen that dihalogen-derivatives of a sulphoneacetic acid, if formed at all, immediately decompose into dihalogen derivatives of sulphones and carbonic anhydride.

α-Phenylsulphonepropionic acid, $SO_2Ph \cdot CHMe \cdot COOH$, is prepared by heating ethyl α-bromopropionate with sodium benzenesulphinate (equal mols.) for 1 to 2 days in alcohol using a reflux condenser; the alcohol is evaporated, water added, and the ethyl salt thus separated, washed and saponified with aqueous soda. The acid crystallises in aggregates of minute, white, monosymmetric or asymmetric needles, melting at 115—116°, and soluble in the usual solvents. The *sodium salt*, the *barium salt* (with 2 mols. H_2O), and the *ethyl salt* are described.

α-Phenylsulphone-α-bromopropionic acid is obtained by the action of bromine on the last-mentioned acid in ether or water at the ordinary temperature; it crystallises in small, thick, lustrous prisms and very slender needles, melting at 134°, and soluble in most solvents.

Ethylidenebromophenylsulphone, $CHMeBr \cdot SO_2Ph$, is obtained, together with carbonic anhydride, when the aqueous solution of the above is heated; it crystallises in rhombic, rectangular tables melting at 49—50°, and is soluble in alcohol and benzene.

Attempts to make α-phenylsulphonepropionic acid by heating ethyl phenylsulphonacetate with sodium and methyl iodide in alcohol failed (compare Abstr., 1889, 994).

α-Paratolylsulphonepropionic acid, prepared similarly to α-phenylsulphonepropionic acid, forms colourless crystals melting at 37°.

The ultimate product of the action of bromine on ethyl phenylsulphonacetate and on paratolylsulphonacetate at 90° is dibromomethylphenylsulphone and dibromomethyltolylsulphone respectively. Chlorine has no action on these ethyl salts.

When phosphorus pentachloride and phenylsulphonacetic acid are mixed together in molecular proportion, phosphorus oxychloride and phenylsulphonacetic chloride (m. p. 58°) are formed. When 2 mols. of the pentachloride and 1 mol. of the acid are heated together at 110°, phosphorus trichloride, phosphorus oxychloride, and a crystalline mass, probably phenylsulphonedichloracetic chloride, $SO_2Ph{\cdot}CCl_2{\cdot}COCl$, are obtained; but when treated with water, the crystalline mass evolves carbonic anhydride and is converted into dichloromethylphenylsulphone.

The author concludes with some remarks as to the analogy between the ketonic acids and sulphone acids (compare Abstr., 1888, 360, 577).

The crystallography of sodium benzenesulphinate and propylphenylsulphone is incidentally described in the paper. A. G. B.

"Methylsaccharin," or Methylbenzoic Sulphinide. (*Chem. Centr.*, 1889, ii, 795—796; from *German Patent* 48583 *of the Badische Anilin- und Sodafabrik*, 1889).—The following new method has been applied to the preparation of Remsen and Fahlberg's sulphinides:—

"*Methylsaccharin*," or *methylbenzoic sulphinide*, has been prepared by it, and its preparation exemplifies the method.

100 kilos. of paratoluidinemetasulphonic acid [$Me : SO_3H : NH_2 = 1 : 3 : 4$] is converted into the diazo-compound, and this is mixed with water and gradually transferred to an almost boiling solution of 48 kilos. of cuprous cyanide, 104·5 kilos. of potassium cyanide, and 500 kilos. of water. After the violent evolution of nitrogen has ceased, the solution is heated a short time to boiling, and then just sufficient sulphuric acid added to decompose the potassium cyanide, when the whole of the cuprous cyanide is precipitated. The hydrogen cyanide liberated is collected in solution of potassium hydroxide. The solution is filtered from the cuprous cyanide, and concentrated until crystallisation commences. The potassium salt of *toluenecyanosulphonic acid* crystallises out in deep-yellow, lustrous prisms, containing water of combination. The salt is readily soluble in water, but only sparingly in alcohol, which renders a dilute alcohol of advantage for purifying it.

To obtain the *sulphochloride*, $CN{\cdot}C_6H_3Me{\cdot}SO_2Cl$, the potassium sulphonate is completely dehydrated by heating at 100—110°; it is then mixed with an equal weight of phosphorus pentachloride and heated in a reflux apparatus at about 100°. The reaction takes place at once; the mass froths slightly at first, then becomes a limpid liquid. The contents of the retort are next heated somewhat higher, in order to

distil off the phosphorus oxychloride, after which it is allowed to cool and solidify. The potassium chloride is extracted by agitating the ground-up product with water several times, after which the residue is dried and recrystallised from light petroleum. It melts at 67°.

The sulphochloride is next converted into the *sulphonamide* by the action of ammonia. Either aqueous, alcoholic, or gaseous ammonia is applicable. It is extremely insoluble in water and methylated spirit. From boiling pyridine, it crystallises in white plates. It dissolves readily in cold water containing free alkali.

Methylbenzoic sulphinide, $C_6H_3Me<{SO_2 \atop CO}>NH$, is prepared from the sulphonamide by hydrolysis with water. 10 kilos. of the sulphonamide is dissolved in 50 kilos. of hot water, by means of just sufficient sodium hydroxide for its complete solution. This solution is then boiled in a reflux apparatus for 4—5 hours, and allowed to cool. The addition of an acid to the solution now precipitates the sulphinide as a white, crystalline powder. It is only requisite to crystallise the crude product once from water in order to obtain colourless, lustrous crystals, melting at 246°. In cold water it is very insoluble, but is much more readily soluble in hot water. Like benzoic sulphinide ("saccharin"), it tastes extremely sweet, and may be applied to the same purposes. If too much alkali is used for the solution of the sulphonamide, the product obtained after hydrolysis will be found to be an acid, and to have lost all the properties of the sulphinide.

J. W. L.

Synthesis of Indigo from Bromacetanilide. By W. FLIMM (*Ber.*, 23, 57—60).—The action of potash on bromacetanilide varies according to the conditions under which it takes place. Thus aqueous potash splits it up into its constituents, some phenylcarbamine being also formed, whilst alcoholic potash converts it into diphenyldiketopiperazine (Abenius, Abstr., 1889, 134). If, however, a mixture of the anilide and solid potash be fused together in small quantities, until a homogeneous, reddish-brown melt is obtained, the latter dissolved in water, and a little ammonia or ammonium chloride solution added, indigo speedily separates out. The melt may also be dissolved in hydrochloric acid, and ferric chloride added, in which case the indigo separates at once. The compound gives all the characteristic reactions of indigo, and shows the same absorption spectrum. The yield is, however, small, amounting only to 4 per cent. of the anilide employed.

It would appear probable that the compound first formed from monobromacetanilide is indoxyl, $C_6H_4<{NH\text{——} \atop C(OH)}>CH$, or pseudindoxyl, $C_6H_4<{NH \atop CO}>CH_2$, and that this then undergoes oxidation with formation of indigo.

Bromacetoparatoluidide is converted on similar treatment into *dimethylindigo*. This can scarcely be distinguished externally from indigo, but yields paratoluidine on distillation with excess of potash.

The following compounds were also subjected to the same treatment,

but did not yield corresponding compounds: bromaceto-α-naphthalide, bromaceto-β-naphthalide, bromacetodiphenylamine, and bromaceto-orthotoluidide. H. G. C.

Symmetrical Diphenyltrimethylene Cyanide and Symmetrical Diphenylglutaric Acid. By N. ZELINSKY and M. FELDMANN (*Ber.*, **22**, 3289—3293; compare Abstr., 1889, 692).—*αα-Diphenyltrimethylene cyanide*, $CH_2(CHPh{\cdot}CN)_2$, is obtained when finely divided, anhydrous sodium hydroxide (8 grams) is added, in small portions at a time, to a mixture of benzyl cyanide (23·4 grams) and methylene iodide (26·8 grams) and the mixture heated, gently at first, and then more strongly to complete the reaction. The oily product is extracted with ether, the unchanged benzyl cyanide and methylene iodide removed by distilling with steam, and the residual diphenyltrimethylene cyanide recrystallised from alcohol. The yield of the pure product is 8 grams, and considerable quantities remain dissolved in the alcoholic mother liquors. It forms well-defined rhombic crystals, $a : b : c = ? : 1 : 0·4877$, melts at 70—71° and its molecular weight, determined by Raoult's method in glacial acetic acid and in benzene solution, was found to be in accordance with the formula given above.

Diphenylglutaric acid, $CH_2(CHPh{\cdot}COOH)_2$, prepared by hydrolysing the preceding compound with alcoholic potash, crystallises from hot water in small needles melting at 164.° F. S. K.

Fichtelite. By E. BAMBERGER and L. STRASSER (*Ber.*, **22**, 3361—3368; compare Abstr., 1889, 714, and HELL, *ibid.*, 614).—The author has carefully determined the boiling point of this compound, using a Zincke thermometer with the mercury column in the vapour. In this way the boiling point was found to be 355·2° at 719 mm., 235·6° at 43 mm. and 233·6° at 42 mm. In the previous determinations by the author and by Hell of the vapour density of fichtelite, made in air by V. Meyer's process, the numbers obtained varied between 7·37 and 7·77, but both observers noticed an apparent partial oxidation. The author has therefore repeated the vapour-density determinations in pure dry nitrogen, and obtained the numbers 8·66 and 8·72, no sign of decomposition being observed. This number agrees very closely with that (8·58) required for $C_{18}H_{32}$, the formula previously adopted by the author as the most probable one. This formula would correspond with a perhydride of retene, and its correctness is made more probable by the fact that fichtelite and retene are so often found together in peat moors. Liebermann and Spiegel have lately obtained (Abstr., 1889, 720) retene dodecahydride, $C_{18}H_{30}$, by the action of hydriodic acid and phosphorus on retene at about 250°, but were then unable to obtain the perhydride (compare next Abstr.). In his previous communication (*loc. cit.*), the author described a substance which he obtained by heating fichtelite with iodine, and which he believed to be dehydrofichtelite. He has now further investigated this reaction. When 27 grams of iodine and 25 grams of fichtelite were heated together, evolution of hydrogen iodide began at 120° and became very energetic at 150°. After keeping the mixture at 200° until evolution of gas ceased, and subsequent purification, *dehydro-*

fichtelite, $C_{18}H_{30}$, was obtained as a clear, colourless, thick oil having a beautiful pale-blue fluorescence. Under 38 mm. pressure it boils at 224—225° (corr.), and under atmospheric pressure (714 mm.) at 344—348° (corr.), but in the latter case slight decomposition takes place. Vapour density determinations carried out in air gave numbers varying between 6·15 and 8·16, but the compound showed signs of decomposition; in pure dry nitrogen, the vapour densities found were 8·59 and 8·85, theory requiring 8·51. The same substance seems to be formed, although in little more than traces by the action of sulphur and of zinc-dust on fichtelite at high temperatures. The properties of this dehydride seem to correspond with those of retene dodecahydride, except that attempts to obtain retene from it proved unsuccessful. Liebermann and Spiegel state that they obtained retene by distilling the dodecahydride with zinc-dust, but that the yield was very small, and the authors' want of success may very probably be owing to the small quantity of substance they had to treat. The lower boiling point given by Liebermann and Spiegel was uncorrected, and so corresponds very closely with that found by the authors. By further treatment of the dehydride with iodine, a *detetrahydride* boiling at 230° under 38 mm. pressure was obtained, but no lower hydrides could be isolated. When spongy platinum was suspended in the boiling dehydride, and a current of oxygen passed through the liquid, oxidation took place, and from the products a small quantity of a heavy oil boiling about 330° and soluble in glacial acetic acid was isolated; this, when oxidised with chromic acid, yielded an *orthodiketone* crystallising in small, red needles. The quantity, however, was too small to establish with certainty its identity with retenequinone.

These results, although not conclusive, leave little doubt that fichtelite is retene perhydride, $C_{18}H_{32}$. L. T. T.

Constitution of Fichtelite. By L. SPIEGEL (*Ber.*, **22**, 3369—3371; compare preceding abstract).—In the preparation of considerable quantities of retene dodecahydride (Liebermann and Spiegel, Abstr., 1889, 720), the author, by strongly cooling the dodecahydride, obtained small quantities of glistening crystals melting at 48°. The same substance seems to be formed when the dodecahydride is treated with phosphorus and hydrogen iodide. Although the author has not yet obtained enough of this substance for absolute proof, there seems little doubt that it is identical with fichtelite, which must, therefore, be retene perhydride. L. T. T.

Behaviour of $\alpha\beta$-Dinaphthylamine when Combining with Diazobenzene. By P. MATTHES (*Ber.*, **22**, 3344—3348).—When an acetone solution of $\alpha\beta$-dinaphthylamine is added to a solution of diazobenzene, in the presence of sodium acetate, *α-benzeneazo-$\alpha\beta$-dinaphthylamine*, $N_2Ph\cdot C_{10}H_6\cdot NH\cdot C_{10}H_7$ [NH : N_2Ph = 2 : 1], is alone formed, but when the reaction is carried out in the presence of hydrochloric acid at 40—50°, besides this $\alpha\alpha\beta$-compound, *α-benzeneazo-$\beta\alpha$-dinaphthylamine* [NH : N_2Ph = 1 : 4], and a *disazo*-derivative, $N_2Ph\cdot C_{10}H_6\cdot NH\cdot C_{10}H_6\cdot N_2Ph$ [NH : N_2Ph = 2 : 1 and NH : N_2Ph =

1 : 4] are also formed. The disazo-compound is much less soluble in alcohol than the two azo-derivatives, and can be thus separated from them. It crystallises in long, woolly, violet needles melting at 238°. This compound is also formed by the action of diazobenzene chloride on either of the azo-derivatives, if enough solvent is used to keep these sparingly soluble substances in solution. When boiled for some time with glacial acetic acid, it is coverted into the *azine*,

$$C_{10}H_6<\overset{N}{\underset{N}{|}}>C_{10}H_5\cdot N_2Ph \ [N : N = 1 : 2 \text{ and } N : N : N_2Ph = 1 : 2 : 4].$$

This crystallises in brownish-yellow woolly needles sparingly soluble in the usual solvents and melting at 287°; by reducing agents it appears to be converted into a eurhodine, which, however, has not yet been isolated.

The separation of the azo-compounds is more difficult, as their solubility in most solvents is very similar. The 1 : 2-compound is, however, less soluble in benzene than the 1 : 4-derivative, and can be obtained pure when crystallised from that solvent; it forms long, woolly, intensely red needles melting at 167°. When treated with mineral acids, it is converted into an *azine*. The 1 : 4-compound cannot be obtained pure directly from the mother liquor; the best way is to dissolve the mixed azo-compounds in acetic acid and treat with hydrochloric acid. The 1 : 2-derivative is thus changed into the azine, whilst the 1 : 4-derivative is converted into its hydrochloride. The two are then precipitated with water, and separated by means of alcohol, in which the hydrochloride is easily soluble, the azine almost insoluble; the azo-base is then liberated by means of ammonia. It crystallises from alcohol in short, thick, yellowish-red prisms melting at 137°. L. T. T.

α-Naphthylamine- and α-Naphthol-ε-Disulphonic Acids. By A. Bernthsen (*Ber.*, **22**, 3327—3335).—When the mixture of 1 : 4′- and 1 : 3′-naphthalenedisulphonic acids, obtained by sulphonating naphthalene in the cold with chlorosulphonic acid or with fuming sulphuric acid containing 35 per cent. of sulphuric anhydride, is nitrated and the resulting nitro-acids reduced, two isomeric α-naphthylaminedisulphonic acids (δ- and ε-) are formed. These can be separated by fractional crystallisation of the normal sodium salts, inasmuch as the normal sodium salt of the so-called Schöllkopf or α-naphthylamine-δ-disulphonic acid [$NH_2 : SO_3H : SO_3H = 1' : 1 : 4'$] (German patent 40571) is relatively sparingly soluble in water, whilst that of the ε-acid remains in the mother liquors, and is best obtained by treating these with excess of hydrochloric acid, which converts it into the less soluble but well crystallised sodium hydrogen salt (Actiengesellschaft für Anilinfabrikation, German patent 45776). *α-Naphthylamine-ε-disulphonic acid*, $NH_2\cdot C_{10}H_5(SO_3H)_2 + 3H_2O$, which can also be obtained by nitrating pure 1 : 3′-naphthalenedisulphonic acid, and reducing the resulting nitro-acid (Ewer and Pick, G. P.-A., E. 2318; Badische Anilin- und Sodafabrik, G. P.-A., B. 9514), crystallises in colourless, lustrous scales and is extremely soluble in hot, sparingly soluble in cold water; the *sodium* salt, with 6 mols. H_2O, crystallises in long needles or thin prisms, and is extremely

soluble in water; the *sodium hydrogen* salt, with 2 mols. H_2O, crystallises in long needles or thin prisms; the *barium* salt crystallises with 3 mols. H_2O in bright-yellow aggregates of needles, and with 4 mols. H_2O in colourless, lustrous, flat needles, and is readily soluble in hot, sparingly soluble in cold water; the *barium hydrogen* salt, with 5 mols. H_2O, crystallises in white, microscopic needles and is sparingly soluble in cold water. The diazo-acid is readily soluble in water, but its sodium salt is sparingly soluble and crystallises in spherical aggregates of small, white needles.

α-Naphthol-ε-disulphonic acid is formed when the diazo-compound of the naphthylamine acid is boiled with dilute sulphuric acid. Its *sodium* salt, $OH{\cdot}C_{10}H_5(SO_3Na)_2 + 6H_2O$, crystallises in long, colourless prisms, is soluble in 5·5 parts of water at the ordinary temperature, is precipitated from its concentrated aqueous solution by addition of salt, and gives a deep blue colour with ferric chloride. Concentrated nitric acid oxidises it readily, but does not convert it into a compound resembling naphthol-yellow. The azo-dyes derived from α-naphthol-ε-disulphonic acid are characterised by their purity of shade and by the fact that they crystallise well; the dye obtained by combination with aniline is orange-yellow; with xylidine, ponceau; with α-naphthylamine red; and with benzidine, violet.

Naphthasultonsulphonic acid ε (naphthalenesulphonelactonesulphonic acid ε; β-naphthol-αβ-disulphonic acid of G. P.-A., E. 2318; ζ-naphtholdisulphonic acid of G. P.-A., B. 9514) is obtained when diazonaphthalenedisulphonic acid ε is boiled with water and a small quantity of sulphuric acid only long enough to expel all the nitrogen, and then at once rapidly cooled. In this way, long slender needles of the *sodium* salt, $C_{10}H_5SO_3{\cdot}SO_3Na + 3H_2O$, are obtained, which, after drying at 110°, have the composition $C_{10}H_5SO_3{\cdot}SO_3Na$. This salt requires 93 parts of water for its solution in the cold, but it is more soluble in hot water, is precipitated from a 1 per cent. solution by the addition of salt, gives no colour with ferric chloride, and is not affected when boiled for a short time with concentrated nitric acid. The *barium* salt crystallises in long, colourless needles and is insoluble in cold water; the *acid* crystallises in silky needles and melts at 241°. When treated with alkalis or alkaline carbonates, naphthasultonsulphonic acid ε is rapidly converted in the cold or at once on warming into α-naphthol-ε-disulphonic acid; on treatment with ammonia, however, it forms *α-naphtholsulphonamidsulphonic acid* ε, $OH{\cdot}C_{10}H_5(SO_3H){\cdot}SO_2NH_2$, which differs from the naphthol-ε-disulphonic acid in yielding azo-dyes having a distinctly redder or bluer shade. The sulphonamidsulphonic acid crystallises in compact needles, or long, slender prisms, and is somewhat readily soluble in cold water; the *sodium ammonium* salt, $C_{10}H_8NS_2O_6Na,NH_3 + H_2O$, forms small, compact crystals and is very soluble in water; the *barium* salt, $(C_{10}H_8NS_2O_6)_2Ba + 5H_2O$, is sparingly soluble in cold water.

The author assigns the constitution $[NH_2 : SO_3H : SO_3H = 1' : 1 : 3']$ to α-naphthylamine-ε-disulphonic acid since (1) it is obtained by the nitration of the 1 : 3′-naphthalenedisulphonic acid; (2) it contains its NH_2-group in an α-position, inasmuch as it yields α-naphthylamine

on distillation with lime; and (3) it yields a sultone (sulphonelactone), a reaction hitherto obtained only in the case of the 1 : 1′ naphthol-sulphonic acid (Erdmann, Abstr., 1889, 157). W. P. W.

Note by Abstractor: The constitution assigned by Bernthsen to so-called α-naphthylamine-ε-disulphonic acid has been confirmed by Armstrong and Wynne (Proc., 1890, 16). W. P. W.

α-Naphthylamine-ε-disulphonic Acid. By G. Schultz (*Ber.*, **23**, 77).—In Bernthsen's paper (preceding Abstr.), it is stated that α-naphthylamine-ε-disulphonic acid [$NH_2 : SO_3H : SO_3H = 1' : 1 : 3'$] is obtained by the reduction of the nitro-acids obtained by nitrating naphthalenedisulphonic acids produced by the sulphonation of naphthalene by three different methods. The author points out that in each of these cases 1 : 3′-naphthalenedisulphonic acid is present and undergoes nitration, and that therefore one method alone exists for the production of α-naphthylamine-ε-disulphonic acid.

In addition to α-naphthylamine-ε-disulphonic acid, other naphthylaminedisulphonic acids are produced when 1 : 3′-naphthalenedisulphonic acid is nitrated, and the nitro-acids reduced; one of these the author has examined and finds to be a β-naphthylaminedisulphonic acid. Further details are promised. W. P. W.

New Class of Diketones. By A. Béhal and V. Auger (*Compt. rend.*, **109**, 970—973).—The authors have previously shown that methylmalonic and ethylmalonic chlorides react with hydrocarbons of the benzene series, with formation of diketones of the type R·CO·CHX·CO·R. The best results were obtained by mixing 500 grams of metaxylene with 80 grams of ethylmalonic chloride, and adding about 160 grams of aluminium chloride in quantities of 20 grams at a time. When the reaction becomes less energetic, the mixture is heated at 60° for two hours. The product after purification crystallises from alcohol of 95 per cent. in confused needles which melt at 63°, and have the composition $C_{13}H_{14}O_2$. It is probably *methyldihydrometanaphthaquinone*

$$[Me : O : H,Et : O : H_2 = 1' : 1 : 2 : 3 : 4].$$

All the products formed by methylmalonic chloride or ethylmalonic chloride under similar conditions will have the same general constitution. With ammonia and the alkaline hydroxides or carbonates, they all give an intense red coloration, which is due to the hydrogen attached to the carbon between the two ketonic groups, for if this hydrogen is displaced by ethyl the coloration is not produced. The chromogenic power also disappears if the diketone is oxidised by a ferricyanide in presence of an alkali.

With hydroxylamine, the diketone yields a dioxime which crystallises in aggregations of needles, and melts at 235° with some previous decomposition. When heated with baryta-water at 195—200°, the diketone yields monobasic *methylbutylphenylacetic acid*, which melts at 74°, is only slightly soluble in water, and crystallises with difficulty. When this acid or the original diketone is oxidised, it

yields propionic acid and bibasic *methylcarboxyphenylacetic acid*, $COOH\cdot C_6H_3Me\cdot CH_2\cdot COOH$, melting at 178°. When the latter is heated at its melting point, it loses carbonic anhydride, and yields a dimethylbenzoic or a methylphenylacetic acid melting at 113—114°.

C. H. B.

Compounds of the Euxanthone Series. By E. PHOMINA (*Chem. Centr.*, 1889, ii, 762; from *Arch. sci. phys. nat. Genève* [3], **21**, 429—440)—In continuation of the author's researches on the hydroxyketones, he finds that potassium hydroxide converts the ketone oxides into dihydroxyketones of the general formula $OH\cdot C_xH_{y}\cdot CO\cdot C_xH_y\cdot OH$. Attempts to substitute hydrogen for the "ketone" oxygen by reducing agents such as hydrogen iodide or zinc-dust proved fruitless.

β-Hydroxynaphthylhydroxyphenyl ketone, $OH\cdot C_{10}H_6\cdot CO\cdot C_6H_4\cdot OH$, melts at 168—169°, and dissolves in organic solvents, but is insoluble in water. The potassium salt crystallises in minute, sulphur-yellow needles. The *dimethyl ether* melts at 66—68°, and dissolves in organic solvents, from which it crystallises in small plates. The *diethyl ether*, which melts at 138—141°, is soluble in alcohol and benzene, crystallising from the latter in plates. The product from benzene appears to be impure. The *diacetate* melts at 107—108°, and crystallises in plates from alcohol. The *hydrazone* melts at 198°. The *oxime* melts at 187—188°, and is soluble in alcohol and benzene.

Hydroxy-α-naphthylhydroxyphenyl ketone, $OH\cdot C_{10}H_6\cdot CO\cdot C_6H_4\cdot OH$, melts at 64—66°, and is readily soluble in benzene and alcohol. The *diacetate* melts at 135—137°. and crystallises in yellow plates. The *oxime* melts at 195—196°, and dissolves readily in alcohol and benzene.

Hydroxytolylhydroxyphenyl ketone, $OH\cdot C_6H_3Me\cdot CO\cdot C_6H_4\cdot OH$, is an oil, and its derivatives appear also to be oils; they were not analysed.

J. W. L.

Tertiary Pyrrolines. By G. DE VARDA (*Gazzetta*, **18**, 546—548).—In a preceding communication (Abstr., 1889, 57), the author showed that 1-methylacetylpyrroline yields 1-methylpyrrylglyoxylic acid on oxidation with potassium permanganate. In order to determine the position of the acetyl and of the glyoxylic residue, the acid was brominated by Ciamician and Silber's method, with a view to its subsequent transformation into methyldibromomaleïmide. The product described was supposed to be 1-methyldibromopyrrylglyoxylic acid; this composition is now confirmed by analysis.

On adding the brominated acid to 10 times its weight of fuming nitric acid, heating, and diluting with water, an oil separates, which may be removed by distillation in a current of steam, leaving a turbid liquid; on cooling, the latter deposits long, colourless needles which melt at 121° to a faintly yellow liquid, and exhibit all the properties of methyldibromomaleïmide. The two atoms of bromine in 1-methyldibromopyrrylglyoxylic acid therefore occupy the positions 3 : 4; 1-methylacetylpyrroline and its product of oxidation, 1-methylpyrrylglyoxylic acid, must therefore contain the acetyl or glyoxyl residue in one of the positions 2 or 5.

1-*Methyltribromopyrrylglyoxylic acid.*—By prolonged boiling of an acetic acid solution of 1-methylpyrrylglyoxylic acid with a large excess of bromine, a yellow, crystalline product is formed, which after repeated recrystallisation still contains more than 2 atoms of bromine; the author considers this product to be a mixture of 1-methyl-di- and tribromopyrrylglyoxylic acids. S. B. A. A.

Phenanthridine. By A. PICTET and H. J. ANKERSMIT (*Ber.*, **22**, 3339—3344).—*Phenanthridine*, $\begin{array}{l} C_6H_4\cdot CH \\ \mid \quad\quad \| \\ C_6H_4\cdot N \end{array}$, was obtained by passing the vapour of benzylideneaniline, CHPh:NPh, through an iron tube filled with pumice and heated to bright redness or nearly to whiteness. It crystallises in long, white needles, melts at 104°, and boils above 360°. It is slightly soluble in boiling water, readily so in alcohol, ether, carbon bisulphide, chloroform, and benzene, and is somewhat volatile in steam. Its aqueous solution shows a slight blue fluorescence. When cold it is odourless, but its vapour is pungent, though less so than that of acridine. It is a tolerably strong base, and yields yellow and mostly crystalline salts, which are more soluble, less coloured, and not so fluorescent as the corresponding acridine salts. The *hydrochloride* forms broad needles, the *nitrite* yellow crystals. Phenanthridine forms no nitrosamine, and is therefore a tertiary base. The *platinochloride* crystallises in needles which are still solid at 225°; the *aurochloride* in prismatic needles almost insoluble in boiling water; the *mercurochloride* in prisms or needles melting at 190°; the *picrate* in thin needles still solid at 220°; the *dichromate* in hair-like needles easily soluble in hot water; the *methiodide* in thick prisms melting at 199—201°; and the *methochloride platinochloride*, $(C_{13}H_9N,MeCl)_2PtCl_4$, forms a nearly white precipitate.

Phenanthridine thus resembles its isomeride, acridine, very closely, the principal difference being in the behaviour of the two substances with reducing agents, acridine yielding a non-basic derivative, and phenanthridine a hydro-base which crystallises in white needles melting at 100°; it has not yet been analysed.

In preparing acridine salts for comparison, the authors found the melting point of acridine mercurochloride to be 225°. L. T. T.

Cinnamylcocaïne occurring naturally in Coca Leaves. By F. GIESEL (*Chem. Centr.*, 1889, ii, 765; from *Pharm. Zeit.*, **34**, 516).—The author has isolated cinnamylcocaïne from the crude bases. Its properties agree completely with those of the synthetically prepared specimens. It differs from cocaïne in its high melting point, 121°, and in its decomposition with potassium permanganate, in which case benzaldehyde is formed. Hydrolysis is effected by hydrogen chloride, when ecgonine and cinnamic acid are formed quantitatively. The author recommends the reaction with potassium permanganate as a sure means of detecting this base in commercial samples of cocaïne. The amorphous isatropylcocaïnes would not be included in this reaction, but could hardly be present in a well-crystallised

specimen of cocaïne (compare Abstr., 1889, 186, 283, 419; this vol., p. 310). J. W. L.

Brieger's Typhotoxine. By L. DE BLASI (*Gazzetta*, **18**, 521—527). —To determine whether the ptomaïne obtained by Brieger from the broth cultures of Eberth's bacillus is due to the specific action of that organism, or only to the action of heat and acids on the albuminoïds, three portions of a slightly alkaline sterilised beef extract were taken, and to two of these (A and B) a pure culture of Eberth's bacillus was added, and to the third portion (C), a pure culture of *Micrococcus candidans;* they were then allowed to remain at a temperature of 37° for 40 days and treated as follows:—

A.—This portion was directly extracted first with ether and then with chloroform; the ethereal extract was treated with water, acidified with a few drops of hydrochloric acid, the solution made alkaline with soda, again extracted with ether, washed, and distilled. On acidification, the residue gave a slight greenish coloration with phosphomolybdic acid, a reddish-yellow precipitate with potassiomercuric iodide, a yellow precipitate with a solution of iodine in potassium iodide, and a white precipitate with mercuric chloride, but no reaction was obtained either with tannin, platinic chloride, or potassiobismuth iodide.

No indication of the presence of any alkaloïdal compound was obtained either from the ethereal distillate or from the chloroform extract.

B was treated by Brieger's method, and the alcoholic extract divided into two parts. In one of these, platinic chloride produced no precipitate, but auric chloride yielded a precipitate of yellowish, hexagonal prisms containing 40·38 per cent. of gold. The other portion was freed from alcohol, and the residue taken up with water. The solution gave precipitates with phosphomolybdic acid, potassiomercuric iodide, potassiobismuth iodide, and with a solution of iodine in potassium iodide. Tannin produced no effect.

C was treated by Brieger's method. The alcoholic extract gave no precipitate with either platinic or auric chloride; the aqueous solution yielded a slight brown precipitate with a solution of iodine in potassium iodide, but did not react with any of the other reagents.

On inoculating a guinea-pig with an aqueous solution of the extract from B, pathological symptoms were developed identical with those described by Brieger; inoculation with the extract from the micrococcus culture gave rise to no morbid symptoms whatever. The author concludes that the method of direct extraction is valueless for the isolation of any definite alkaloïd, but that Brieger's method is efficient, and that the negative result obtained from the culture of the non-pathogenic organism demonstrates that typhotoxine is either the direct product of the activity of Eberth's bacillus, or is due to the secondary action of heat and acids on some unstable substance produced by that bacillus. The results of inoculation with the substances extracted from the culture of *M. candidans* prove that the action of heat and acids was ineffectual to produce any toxic substance from it. S. B. A. A.

Composition of Albumin. By E. HARNACK (*Ber.*, **23**. 40—43). —The author has determined the amount of sulphur contained in the albumin free from ash, the preparation of which he has recently described (this vol., p. 272), and finds, as a mean of five closely agreeing analyses, that it contains 1·91 per cent. This number is higher than the one previously obtained by the author, but agrees with that found by Lieberkühn, and also by Loew (*Pflüger's Archiv*, **31**, 393); and the empirical formula suggested by the latter, namely, $C_{210}H_{330}N_{52}O_{66}S_3$, is regarded as the most probable.

A comparison of the number of sulphur-atoms and the number of carbon-atoms in the different albuminoïds, according to the present analysis, shows a very curious relation—

Thus in egg-albumin	there is 1 atom of	sulphur	to	70	of carbon.
,, globulin	,,	,,	,,	146	,,
,, hæmoglobin	,,	,,	,,	350	,,

or the numbers of carbon-atoms present for each sulphur-atom in these three compounds are in the almost exact proportion of 1 : 2 : 5. Whether this simple relation is due to chance or not, can only be ascertained by a long series of further investigations. H. G. C.

Physiological Chemistry.

Respiration in the Horse during Rest and Work. By F. SMITH (*J. Physiol.*, **11**, 65—78).—Recently Zuntz and Lehmann (*Zeit. wiss. Landwirthsch.*, **18**) have published a paper on this subject. They placed the horse on what was practically a treadmill, in order to obtain work. In the present research, 35 horses were used, and 250 experiments made in all. A closely-fitting mask was fitted on the horse's face; this was connected by tubes with a meter to measure the gases; the expired air was collected, and for the analysis Hempel's apparatus with absorption pipettes was used. In one series of experiments, A, water was used as a confining medium; in another series, B, mercury was employed instead. The horse was allowed to perform natural work: walking, trotting, galloping, &c.; and immediately after coming in, the mask was adjusted, and an observation made. The mask was on for 20—30 seconds in each experiment. This method is regarded as being superior to the method of artificial work produced by Zuntz and Lehmann's moveable platform.

The capacity of a horse's lungs is about 1 cubic foot, the rate of respiration during repose is 9 to 12 per minute; this is accelerated by work in proportion to the severity of the work. The diet employed was 12 lbs. of hay and 10—12 lbs. of oats daily.

The following table gives a summary of the respiratory changes at the different paces:—

	Series.	Air expired per hour in cubic feet.	CO_2 expired per hour in cubic feet.	O absorbed per hour in cubic feet.	Respiratory quotient.	Undetermined gases per hour in cubic feet.
Repose	A....	80·783	1·028	1·566	0·656	0·489
	B ...	67·556	1·234	1·705	0·723	0·368
Walk .	A....	150·588	1·097	2·234	0·491	1·148
	B....	116·520	1·058	1·843	0·574	0·765
Trot. ..	A....	258·000	2·948	5·637	0·523	2·529
	B....	317·738	4·831	7·314	0·660	2·482
Canter	A....	421·598	4·916	7·861	0·625	2·877
	B....	360·400	5·008	8·839	0·566	3 741
Gallop ..	..	849·099	14·972	26·071	0·574	6·695

W. D. H.

Influence of Inorganic Salts on Development. By S. RINGER (*J. Physiol.*, **11**, 79—84).—In a number of communications (*J. Physiol.*, **4**, **5**, **6**, **7**), the author has previously shown the necessity of inorganic salts for sustaining life and vital activity, in muscular contraction, the heart beat, the action of cilia, and the life of fishes. Of these, calcium salts seem the most important, and there is antagonism between the action of these salts and those of sodium and potassium. An excellent fluid for sustaining the heart's beat is made by mixing suitable small proportions of the salts of all these metals; and of the calcium salts, the phosphate appears to be the most effective. A fish which dies in distilled water in a few minutes lives for weeks in river water, which always contains the necessary saline ingredients. In the present researches, the inquiry is extended in order to ascertain whether the same is true for the development of frog's spawn, and the growth of tadpoles, and it was found that it is so. Placed in distilled water, they die in a few hours; the addition of sodium hydrogen carbonate, or of lime-water, or calcium chloride, is insufficient to maintain life. Calcium hydrogen carbonate and tribasic calcium phosphate, on the other hand, sustain life for a considerable time, and development progresses. It would appear that those salts of lime where the base is least saturated by the acid are those most capable of sustaining function. W. D. H.

Method of Raising the Specific Gravity of the Blood. By W. HUNTER (*J. Physiol.*, **11**, 116—120).—After injecting blood into the peritoneal cavity of an animal, the blood corpuscles of the animal become, within an hour or two, apparently much increased in number. This is not a real increase, but is due to the fact that the density of the animal's blood (as determined by Roy's method, Abstr., 1887, 608) is increased. The increase of specific gravity is due to the fact that the injection into the peritoneum sets up irritation, and leads to the transudation of blood plasma from the circulation. Later this subsides, and then there is a real increase in the animal's blood corpuscles, due to absorption of those from the foreign blood

which is injected. The injection of a solution of sodium phosphate, or other neutral salt, similarly raises the specific gravity of the blood; but the effect is not so marked and is more transient.

W. D. H.

Human Chyle. By D. NOËL PATON (*J. Physiol.*, **11**, 109—114).—Very few analyses of human chyle have been recorded. Rees obtained a specimen from a criminal after execution (*Phil. Trans.*, 1842). Specimens have also been obtained in cases where the thoracic duct or the lacteals have ruptured into a serous cavity; here, however, one has to deal with a mixture of chyle and the lymph of the serous membrane. In one of these cases, the analysis was made by Hasebrock (Abstr., 1888, 736).

In the present case, chyle was obtained from a patient in whom the thoracic duct had been cut in an operation for the removal of a tumour of the neck. Systematic observations could only be made at the time when the patient was in an emaciated and dying condition; but from these it was roughly estimated that in health, the flow must have been between 3,000 and 4,700 c.c. in 24 hours, or between 5·2 and 7·9 kilos. per 100 kilos. of body weight. Four specimens were obtained for analysis; the following table gives the results in parts per 1,000:—

Water....................	943 —958
Solids....................	56 — 41
Inorganic.................	6·2 — 6·7
Organic...................	35 — 50
Proteïds..................	11·8 — 13·7
Fats......................	24
Cholesterin...............	0·6
Lecithin..................	0·36

The percentage of solids gradually decreased as the patient became weaker; this was due to a decrease in the organic constituents. The proteïds were present in smaller amount than in previously recorded analyses. The diet given was rich in fats, which accounts for the high percentage of fat in the chyle. W. D. H.

Nutritive Value of Different Albuminoïds. By S. GABRIEL (*Bied. Centr.*, **18**, 807—815; from *J. f. Landw.*, **37**, 175—190).—A wether was fed daily with barley-straw (500 grams containing 3·25 grams of nitrogen) and an amount of albumin containing 9 grams of nitrogen; this latter was mixed with starch in such quantity that the amount of non-nitrogenous extract always remained the same. The experiment was divided into eight periods, in the first seven of which a different albuminoïd was used; in the last, no albuminoïd was given. The substances given daily during the eight periods were as follows:—I, rye (559·00 grams); II, peas (272·73 grams), and starch (302·28 grams); III, conglutin (63·02 grams), and starch (512·32 grams); IV, meat meal (free from fat, 63·65 grams), and starch (512·32 grams); V, albumin (74·87 grams), and starch (512·32 grams); VI, caseïn (71·31 grams), and starch (512·32 grams); VII, glutin (63·38 grams), and starch (512·32 grams); VIII, starch (580·32

grams). In each case the animal had, in addition, salt (8 grams) and water (3 litres); the water which was left was weighed. The urine and fæces were daily collected, weighed, and the nitrogen determined. The amount of nitrogen digested was found by subtracting the amount in the fæces from the amount in the food (12·25 grams); whilst the amount of nitrogen of the albuminoïd food which remained undigested was found by subtracting 4·4 grams (the amount of nitrogen in the fæces during the period (VIII) when no albumin was given) from the nitrogen of the fæces from the other experiments. The results indicate that of the pure albuminoïds (III, V, VI), 12·2 to 15·5 per cent. remains undigested. Stutzer found in artificial digestion experiments for conglutin 0·98 per cent., and for caseïn 8·24 per cent. of the total nitrogen remained undigested. When the amount of nitrogen fixed by the animal (the nitrogen digested less that of the urine) is calculated to a percentage of the total digested nitrogen, great differences are found. The number for meat meal is 41·88, for rye 6·31, and for conglutin, albumin, caseïn, and free albumin 27·70, 32·56, 29·77, and 21·82 respectively. The fact that when glutin, which is not capable of assimilation, was given, the animal not only did not lose, but gained nitrogen, points to the conclusion that the glutin saved the whole of the digestible albumin of the straw from being destroyed and caused it to be deposited.

With regard to the last period where no albumin was given, it was found that the fæces always contained starch; this observation agrees with that of Haubner and others that large amounts of starch are only completely digested when a certain amount of albumin is present.

Neither the nitrogen nor the carbon in different albuminoïds forms a criterion of their nutritive value. Conglutin, which differs most in its composition from other proteïds, approaches albumin and caseïn very nearly. On the whole, the three animal albuminoïds seem to act more favourably than those of vegetable origin; but more experimental evidence is required before generalising this fact.

N. H. M.

Value of Commercial Foods. By W. Knierim (*Bied. Centr.*, **18**, 815—820).—The object of the experiments first described was to determine the relative values of several kinds of cake with regard to the production of milk. The cow received 15 kilos. of clover-hay and 1·5 kilo. of cake. Rape-cake produced an increased amount of milk on the first day; the same was observed with cocoanut-cake. The increase was, in both cases, considerable, and the effect of the cocoanut-cake was more lasting than that of the rape-cake. In other experiments, in which 10 kilos. of green fodder was given, linseed-cake (1·5 kilo.) gave an increase of 12 per cent., and cocoanut-cake raised the yield of milk by 11 per cent.; hemp-cake had no effect at all. Sunflower-cake, poppyseed-cake, and cocoanut-cake (1·5 kilo. in each case) were given, together with meadow hay of bad quality (14 kilos.); in each case the yield of milk was considerably increased—the greatest increase being produced by the cocoanut-, and the least by the sunflower-cake.

Further experiments are described, in which oat-meal, sunflower-cake, cocoanut-cake, and pea-meal (1·5 kilo.) were given, along with a still poorer food, consisting of hay (9 kilos.) and oat-straw (3·5 kilos.). Cocoanut-cake and sunflower-cake gave equally good results; pea-meal was less effective.

In order to determine whether the failure of hemp-cake was due to its being less digestible, experiments were made with bullocks, horses, sheep, and rabbits. The effect on bullocks was comparatively slight. The horses were found to be capable of doing much less work when much hemp-cake was given to them, whilst with sheep the cake was found to be distinctly injurious, causing the animals to become thinner. Rabbits could not be kept alive on hemp-cake alone. It is possible that the cake might give better results when used with less nitrogenous fodder.

Sesame-cake was also found to be a very good milk producer.

Experiments with rabbits showed that cotton-seed-cake and earth-nut-cake are very digestible. N. H. M.

Nutritive Value of Wheat-meal. By A. W. Blyth (*Proc. Roy. Soc.*, **45**, 549—553).—In these experiments, two persons were fed on whole-meal and distilled water for a period of 28 days in one case, and a week in the other, the food and excreta being analysed in each case. The experiment on the first patient consisted of three parts: (1) a period of 8 days, during which the insufficient quantity of 16 ozs. per day of whole-meal was taken; (2) a period of 14 days, during which 20 ozs. per day was taken; and (3) a period of 7 days, during which 28 ozs. per day was taken. In the second case the proportion of whole-meal per day was 16—22 ozs. In the first case there was loss of weight during the first two periods, but a slight increase during the third. In the first period, nitrogen was excreted in excess of that ingested, phosphoric acid was in equilibrium, but more salts were excreted than taken in. In the second period nitrogen and phosphoric acid were in equilibrium, and there was retention of salts. During the third period there was retention of nitrogen, phosphates being in equilibrium. In both cases there was an excretion of sulphates in the urine, and of unoxidised sulphur from the intestinal canal, although the flour only contained traces of sulphur. In the first case, chlorine was excreted in excess of that taken in. The above renders it evident that the sulphur in albumin is of importance as a food, and that the snlphur excreted must have been obtained from sulphur stores in the body. If the excretion of the bowel is considered as waste, then 15·6 per cent. of the nitrogen in food is not assimilable, 37 per cent. of the fat is not digested, and 51·8 per cent. of the ash also passes away. H. K. T.

Occurrence of Mercury in Tapeworms. By L. Oelkers (*Ber.*, **22**, 3316—3317).—Two tapeworms from a syphilitic patient, who had used mercury ointment, were found to show a peculiar grey colour, due to the presence of some mercury compound, probably the oxide or sulphide. F. S. K.

Influence of Nicotine and Atropine on Salivary Secretion. By J. N. LANGLEY (*J. Physiol.*, 11, 123—158).—This paper, which is the sixth in a series of communications on the salivary secretion, relates chiefly to the connections of the nerves which pass to the submaxillary and sublingual glands to various groups of nerve-cells or ganglia in different animals. An important method of determining this point depends on the fact that, whereas atropine paralyses the secretion by affecting the nerve-endings, and has no poisonous effect on nerve-cells or gland-cells, nicotine, on the other hand, produces a somewhat similar effect, by its poisonous effect on nerve-cells; it leaves nerve-fibres and gland-cells intact; this is true, whether the drug be injected into the circulation, or applied locally to the ganglion. W. D. H.

Influence of Sodium Phosphate on the Excretion of Uric Acid. By A. HAIG (*Medico-Chir. Trans.*, **72**, 399—406).—Disodium hydrogen phosphate is a well-known solvent of uric acid, and increases the excretion of that substance. When, however, commercial preparations of the phosphate were employed in cases of gout, it was found that attacks were precipitated, and both in these cases and in healthy persons the amount of uric acid excreted was diminished. Analysis revealed the fact that these preparations contained from 1·2 to 6·8 per cent. of sodium sulphate; it is this impurity which causes the retention of uric acid. The pure phosphate prepared from sodium hydroxide and phosphoric acid acts as stated at the commencement of this abstract.

The addition of a little sodium hydrogen carbonate increases the efficiency of the phosphate in this direction; the addition of acid (such as dilute phosphoric acid, which causes the formation of dihydrogen sodium phosphate) diminishes it. The acid phosphate is another frequent impurity of commercial preparations, and this is an additional reason why the pure salt should be employed. The phosphate and the salicylate (Abstr., 1888, 1322) act differently in relation to acidity of the urine, the excretion of uric acid being hindered by acidity in the former case, accelerated in the latter. In many cases where the powerful effect of salicylate is unnecessary, or its toxic effects are to be feared, the use of the phosphate as a substitute is recommended. W. D. H.

Clay-coloured Stools without Jaundice. By T. S. WALKER (*Medico-Chir. Trans.*, **72**, 257—273).—The object of this paper is to establish the following propositions:—That the presence of the pancreatic juice in the intestines is as essential as that of the bile to produce the brown colour (stercobilin) of the dejections; that clay-coloured stools may, consequently, be caused by disease of the pancreas when the liver is perfectly healthy; that they may be caused either by cutting off the supply of bile as in ordinary obstructive jaundice, or the supply of pancreatic juice; that the bile pigment which appears in the fæces is that only which has been acted on by the pancreatic juice, and that consequently the latter organ has a hitherto unsus-

pected physiological and pathological importance as a factor in the elimination of bile.

These propositions are supported by the records of two cases: *Case* 1 was that of a man who died in his ninety-first year, and who, for 24 years previously, had passed colourless stools; during all this time, except for a few days, jaundice was absent. *Post mortem*, the liver was healthy, the bile-ducts patent, and fresh bile was present in the duodenum. The pancreas, on the other hand, was enlarged, and its duct absolutely impervious, owing to the presence in it of a large stone, about 8 inches long. *Case* 2 was similar; clay-coloured stools occurred for seven years; jaundice was absent. *Post mortem*, liver and bile-ducts healthy; pancreatic duct obliterated, owing to cicatrisation of an old ulcer. In these cases the question arises what becomes of the bile-pigment, and it is suggested that as it is not acted on by pancreatic juice, it is completely reabsorbed.

In conclusion, it is pointed out that Bernard noticed the occurrence of a brown tint when bile was mixed with pancreatic juice; that previous clinical observers have, in a few scattered cases, noted the simultaneous occurrence of clay-coloured stools with pancreatic disease, and that in the fœtus, meconium is coloured by unchanged bile-pigments, not by stercobilin; the pancreas not beginning to secrete until after birth, and the process of absorption being probably also in abeyance until then. W. D. H.

Physiological Action of the Active Principle of Jequirity. By S. MARTIN and R. N. WOLFENDEN (*Proc. Roy. Soc.*, **46**, 94—100).—Klein has shown that the poisonous properties of the seeds of *Abrus precatorius* (jequirity) cannot be due to a bacillus, and Warden and Waddell (Non-bacillar nature of Abrus poison, Calcutta, 1884) showed it to be due to the action of a poisonous proteïd. The proteïds in the seeds are two in number, a globulin and an albumose, and the present paper relates to the physiological action of the first of these. The proteïds were obtained by extracting the crushed seeds with 15 per cent. solution of sodium chloride; they were precipitated from this extract by saturation with ammonium sulphate; the precipitate was redissolved by adding water; and from this solution the globulin was precipitated by dialysis, collected, washed, and dried.

The actions ascribable to this globulin are the production of local œdema and inflammation when subcutaneously injected or applied to the eye, the presence *post mortem* of petechiæ beneath the serous membranes, and the occurrence of hæmorrhagic gastro-enteritis. It also produces a remarkable fall of body temperature after subcutaneous injection, and in lethal doses, it causes rapidity of breathing shortly before death. It has little or no effect on blood pressure. The activity of this globulin is destroyed by heating the solution to 75° or 80°, the temperature at which it enters into the condition of a heat coagulum. W. D. H.

Toxic Action of the Albumose from Jequirity Seeds. By S. MARTIN (*Proc. Roy. Soc.*, **46**, 100—108).—This is a continuation of the research of which the preceding abstract is a *résumé*. The albumose was obtained by precipitating the two proteïds of the seeds

by means of alcohol. The precipitate was allowed to remain under absolute alcohol for several months: the globulin was thus rendered insoluble; the albumose, however, was freely soluble in water after this treatment. It gave the following reactions: The aqueons solution was neutral to litmus-paper, and gave no precipitate on boiling. Acetic acid and also nitric acid gave precipitates which dissolved on heating, and reappeared on cooling. Copper sulphate gave a precipitate soluble in excess of the reagent. Copper sulphate and potash gave a "biuret" reaction. Mercuric chloride gave a precipitate insoluble in excess of the reagent. The symptoms produced by the albumose closely resemble those noticed when the globulin is hypodermically injected. There is gradually increasing weakness, with rapid breathing aud lowering of body temperature, but no convulsions or paralysis. It also causes severe conjunctivitis when applied to the eye. Its poisonous properties are lessened by heating at 70—75°, and completely destroyed at 85°.

The albumose is not, however, so powerful a toxic agent as the globulin, the dose necessary to produce the same effects being larger.

A comparison is drawn between the action of these proteïds and those of other poisonous substances of the same class, especially those in snake-venom.

The following table contrasts the activity of the venom of various snakes and of Abrus:—

Common adder.—Fatal dose in man, 0·0021 gram per kilo. of body weight (Fontana).

Australian tiger-snake.—Fatal dose in dog, 0·00485 gram per kilo. of body weight.

Cobra.—Fatal dose in dog, 0·000079 gram per kilo. of body weight (Vincent Richards).

Abrus poison—

Globulin.—Fatal dose, 0·01 gram per kilo. of body weight.

Albumose.—Fatal dose, 0·06 gram per kilo. of body weight.

Peptic albumoses.—Fatal dose in dog, any dose over 0·3 gram per kilo. of body weight (Pollitzer).

W. D. H.

Acetonuria and Diabetic Coma. By S. West (*Medico-Chir. Trans.*, **72**, 91—110).—A systematic examination of the urine for acetone was made in a number of cases of healthy people, of those suffering from various complaints, and of those suffering from diabetes. The tests employed were le Nobel's or Legal's nitro-prusside test, and Lieben's iodoform reaction. The first was applied to the urine direct, the latter to the distillate from the urine. In addition to these, the red reaction which is given by ferric chloride was sought; whether this is produced by ethyl acetoacetate or some allied compound is at present uncertain. The main results of the investigation were as follows:—Acetone is absent, or almost so in healthy urine. Acetonuria is common in diabetes without coma, and is not constantly present in cases of diabetic coma. It varies greatly in the same case from time to time, without any evident cause. It stands in no relation to the amount of sugar in the urine, but varies independently of variations in the sugar and specific gravity. It is, moreover, often

found in other diseases than diabetes; for instance, in four cases of pneumonia, in one case of cirrhosis of the liver, in one of spinal affection, in one of cerebral hæmorrhage, and in one of delirium tremens.

The iron reaction (? diaceturia), on the other hand, is rare except in cases of diabetes. It may be present when acetone is absent, or absent when acetone is present. They may, however, be both present or both absent at the same time, and neither appears to stand in any definite relation to coma. The presence of acetone in the urine, or the occurrence of the iron reaction is, however, by no means without clinical significance. They indicate defective metabolism, and that the patient is in a worse condition than when the tests applied gave negative results. Acetone and the substance which gives the iron reaction may be bye-products in the formation of the at present unknown poison, and their presence often indicates the presence of this poison and the onset of coma. The occurrence of the iron reaction should be regarded as more serious than that of acetone.

These conclusions confirm in the main those of v. Jaksch (*Acetonuria u. Diaceturie, Berlin*, 1885); the terms acetonæmia and acetonuria are misleading if used as synonymous with diabetic coma.

W. D. H.

Pernicious Anæmia. By F. W. MOTT and S. A. VASEY (*Lancet*, 1890, **1**, 287—289).—In a case of pernicious anæmia previously recorded (*Lancet*, 1889, **1**, 520), it was noted that the urine had a high colour, although its specific gravity was low, and that the liver *post mortem*, on staining sections with potassium ferrocyanide and hydrochloric acid, became intensely blue and thus gave evidence of excess of iron. It was therefrom inferred that in the liver the hæmoglobin of the corpuscles is split up into an iron-free pigment of the nature of hydrobilirubin, which passes into the urine as urobilin, and an iron-containing constituent which remains behind in the liver cells.

A case of a precisely similar kind is now related, and the view above stated is fully borne out by the results of analysis:—

	Weight in grams.	Ferric oxide per cent. in organ.	Total ferric oxide in whole organ.	Total ash in organ.	Percentage of ferric oxide in ash.
Anæmic liver..	1240	0·29	3·60	1·05	27·2
,, kidney	282	traces	—	1·25	—
,, spleen.	141	trace	—	0·9	—
Normal liver...		traces, along with distinct traces of copper.	—	1·16	—

An interesting point in addition to the high percentage of ferric oxide obtained from the liver is the low percentage in the spleen. This is especially noteworthy, as the view is very generally held that the spleen is an important site for the destruction of blood corpuscles.

The above analysis, as well as certain experiments of Schäfer, showing the absence of free hæmoglobin in the blood of the splenic vein, lend no support to this doctrine.

Hunter (*Practitioner*, Sept., 1889) has published a similar case to the above. The pigment in the urine in this case was not, as in Mott's case, normal urobilin, but pathological urobilin.

Copeman (*Lancet*, 1890, **1**, 375) records a fourth case of the same nature, and in this, as in Mott's case, the urinary pigment was normal urobilin. W. D. H.

Pfeiffer's Test for Latent Gout. By W. ROBERTS (*Lancet*. 1890, **1**, 9—10).—At the seventh congress of German physicians (Wiesbaden, 1888) Pfeiffer introduced the following urinary test for discovering the condition known as latent gout, and the allied condition uro-lithiasis; the acid urine of the 24 hours is divided into two parts, one part is passed through a filter on which pure uric acid has been placed, the other part is not so treated. An equal volume of each portion is then acidified with strong hydrochloric acid, and set aside until the precipitated uric acid has fully separated. The two precipitates are collected and weighed. In normal urine, the weight is approximately the same in both cases. But in the case of gout, or uro-lithiasis, the portion passed through the uric acid filter is found to have the greater portion of its uric acid removed from it, and little or no formation of uric acid crystals occurs on subsequently treating the filtrate with hydrochloric acid. On repeating these experiments in the present research, the test was found to be most untrustworthy and misleading. Nearly all acid urines desposit a portion of their uric acid upon the pure acid on the filter; but the amount so deposited in normal acid, as well as in gouty urine, depends on the interaction of a number of factors, namely :—the degree of acidity of the urine, its comparative richness in uric acid, the rate of filtration, and the amount of uric acid placed on the filter. A simpler and more trustworthy test consists in placing several portions of the urine in corked phials in a warm place (to prevent precipitation of urates), a few drops of chloroform being added to prevent putrefaction. Sooner or later crystals of uric acid are deposited if the urine is acid; the time at which crystals first make their appearance giving an indication of the degree of precipitability of the urine, that is of its proneness to deposition of uric acid. If crystals generally appear in 2 or 3 hours, this would indicate a morbid imminence of gravel; if only after 12 or 24 hours, the occurrence does not come within the range of pathological significance. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Behaviour of the Vegetable Cell with very Dilute Alkaline Silver Solution. By O. LOEW and T. BOKORNY (*Chem. Centr.*, 1889, ii, 849—850, from *Bot. Centr.*, 1889, 39). The authors have made

several further experiments with the object of determining the cause of this reaction (Abstr., 1888, 983), more especially since Pfeffer (Abstr., 1889, 1028) has concluded that the reducing power is due to albumin tannate or to tannin.

Having observed that if spirogyra be cultivated in solutions of nitrates, a part of the tannin disappears, the authors cultivated *Spirogyra nitida* in a solution containing 1 part of sodium and potassium nitrates, and of sodium and magnesium sulphates in 10,000 parts of distilled water. When sown, the spirogyra contained a fair quantity of starch, fat, and tannin. After allowing the vessel to remain for 12 days in a somewhat shaded part of the room, the algæ were quite healthy, and were, moreover, free from fat and tannin, and contained but little starch. Dilute ammonia caused a considerable precipitate, which was free from fat and tannin, but still reduced silver solution with energy. Thirty per cent. acetic acid, or protracted heating at 70—80° destroyed this reducing power. Since these tannin-free cells contain nothing besides albumin, the authors conclude that the reducing power must be attributed to it, and that the treatment with acetic acid or the process of heating causes such a change in the albumin as to destroy its reducing power. J. W. L.

Occurrence of Iodine in Fucus vesiculosus and Chondrus crispus. By L. VAN ITALLIE (*Arch. Pharm.* [3], **27**, 1132—1134).—By Flückiger's method (Abstr., 1887, 996), a faint iodine reaction was obtained with 3 grams of *Fucus vesiculosus*, and with 10 grams of *Chondrus crispus*. 50 grams of the former plant was extracted with 40 vol. per cent. alcohol, the solution neutralised with sodium carbonate, evaporated to a syrup, this extracted with water, and treated with chloroform; the chloroform remained colourless. The addition of nitrous acid dissolved in dilute sulphuric acid set free its iodine, which amounted to 5·1435 milligrams, or 0·0113 per cent. of the absolutely dry substance, and 0·01029 per cent. of the plant dried over lime. The whole of the iodine was found to be extracted by the above process. The material separated by absolute alcohol gave no reaction for iodine. From these reactions, the author concludes that the iodine is present in *F. vesiculosus* as iodide. The amount of iodine in *C. crispus* was too minute to estimate. Neither plant gave evidence of the presence of bromine. J. T.

Chemical Constituents of Scopola carniolica. By W. R. DUNSTAN and A. E. CHASTON (*Pharm. J. Trans.* [3], **20**, 461—464).—*Scopola carniolica* is a solanaceous plant indigenous to Austro-Hungary. It has lately been exported to this country with a view to its employment in medicine as a substitute for belladonna. The total alkaloïd was extracted from the carefully dried (30—40°) rhizome, no temperature above 40° being employed in the process, and no alkali being used, except very weak ammonia, so that the possibility of the occurrence of any change in the alkaloïds during their extraction was avoided; on crystallising the alkaloïd from ether, pure hyoscyamine (m. p. 108—109°) was obtained. To ascertain whether any other

mydriatic alkaloïd was present, the residue obtained from the ethereal liquid was dissolved in diluted hydrochloric acid, and fractionally precipitated with gold chloride; each fraction was then recrystallised until its melting point was not changed by a repetition of the process. From the eight fractions of precipitate, 27 specimens of recrystallised aurochloride were obtained. With the exception of what was possibly a trace of hyoscine aurochloride, nothing but hyoscyamine aurochloride was found (m. p. 159—162°, corr.). A similar process of fractional precipitation of the aurochloride was conducted with a small quantity of alkaloïd, which had not been extracted by ether from the alkaline aqueous liquid. This yielded only hyoscyamine aurochloride. The salt was identified by its melting point, as well as by the results afforded by its analysis; the alkaloïd was also regenerated from it, and shown to correspond with pure hyoscyamine. The plant is abundant, and would therefore seem to constitute an important source of this alkaloïd. The rhizome is also shown to contain rather more than 0·1 per cent. of cholesterol, melting at 132—133°, and affording analytical results which agree with the formula $C_{26}H_{44}O + H_2O$. When dried at 100°, the crystals lost water, leaving the anhydrous substance, which melts at 137·5°. The benzoate was prepared by dissolving the substance in benzoic chloride, and heating the liquid for 15 minutes near its boiling point. On pouring it into aqueous soda, the benzoate remains insoluble; after purification and crystallisation from ether, it melted at 145·5°. The cholesterol from *S. carniolica* most nearly resembles the phytosterin of Hesse. The substance has not before been obtained from an atropaceous plant, but the authors have since isolated it from *Atropa belladonna*. There were also obtained from *S. carniolica* a fat which is under examination, a crystalline sugar yielding an osazone identical with that of dextrose, and a crystalline substance whose aqueous solution when alkaline is highly fluorescent, and appears to be methylæsculetin. The paper is followed by others in which different observers record the results of therapeutical, botanical, and pharmaceutical examinations of the plant. Therapeutically it appears to have some marked advantages as compared with belladonna. W. R. D.

Analyses of the Seed of Calycanthus glaucus. By H. W. Wiley (*Amer. Chem. J.*, **11**, 557—567).—The analyses cannot be given in full. The seeds were found to contain only a very small quantity of starch, but large amounts of sugars, albuminoïds, and oil: there being as much as 47 per cent. of the latter.

This oil has a faint yellow colour, and a peculiar odour. Its sp. gr. when obtained by extracting the seeds with petroleum = 0·9058; the sp. gr. of the expressed oil = 0·9110 (water at 100° = 1). It is free from volatile acids, gives a fatty acid crystallising at 12·5°, and has a refractive index of 1·47351 at 28° (water at 28° = 1·33338). The crude expressed oil absorbs 129·53 per cent. of iodine, the purified extracted oil 128·66 per cent.

The oil contains an alkaloïd discovered by Eccles, and named by him *calycanthine*. This was obtained from the seeds by powdering them, extracting the fat with petroleum, and digesting the residue

with various liquids, best with dilute sulphuric acid (1 : 50). The sulphuric acid extract is made strongly alkaline with ammonia, and extracted repeatedly with ether; on evaporating the ether extract, calycanthine crystallises in feathery masses on the sides of the dish. The kernels of the seeds contain about 3 per cent. of the alkaloïd, the hulls about 1 per cent. The alkaloïd is insoluble in alcohol and water. With sulphuric acid, it gives a pale-yellow colour, with nitric acid a persistent bright-green, with sulphuric acid and potassium dichromate a fine, blood-brick-red, and with sulphuric acid and cane-sugar a fine purple, persisting for some time, and finally changing to blue. Owing to the presence of sugar in the seed, this last reaction may be obtained by the simple application of sulphuric acid to the raw seed. C. F. B.

Bark of Quina morada (Pogonopus febrifugus, Benth.-Hook.). By P. N. Arata and F. Canzoneri (*Gazzetta*, **18**, 409—421).—The authors have examined a specimen of bark found in Bolivia and in the north of the Argentine Republic, commonly known as "Cascarilla," or "Quina morada," and credited with many of the therapeutic characteristics of the true cinchona bark. For a variety of reasons the authors consider it to belong to the *Pogonopus febrifugus*, *Benth.-Hook.*, syn. *Howardia Wedd*, *rubiacea*, described by Griselbach. In appearance the bark is irregular on the outside and scaly within; the colour varies from yellowish-white to reddish, and is a dirty-white on freshly-exposed surfaces; it is soft and spongy to the touch, a little lighter than water, has a slightly bitter taste, scarcely any odour, and burns very readily, leaving a white ash. It imparts a bluish fluorescence to water with which it has been boiled, and a yellowish-blue fluorescence to alcohol.

Two substances were extracted from this bark, namely, a blue fluorescent substance, moradin, and an alkaloïd, moradëine.

To isolate these, the powdered bark is extracted with alcohol, the extract treated with an alcoholic solution of lead acetate, filtered, freed from lead, and concentrated, when a crystalline deposit of moradin is obtained. The mother liquor is then treated with potash and ether, the ethereal extract treated with hydrogen chloride, and the precipitate of moradeïne hydrochloride purified by again treating it with soda, ether, &c.

Moradin contains no nitrogen, and its formula is either $C_{21}H_{18}O_8$ or $C_{16}H_{14}O_6$. The former agrees better with the composition of the acetyl-derivative, triacetylmoradin.

Moradin crystallises in slender, colourless needles, or in large, anhydrous prisms, and melts at 201—202°. It has the characters of an acid, but none of its salts could be isolated. Alkalis increase, and acids (except acetic) diminish the fluorescence of its solutions. Ferric chloride gives a green coloration and, after a time, a green precipitate; gold chloride gives a blue coloration and green precipitate. It is dissolved by concentrated sulphuric acid, forming a yellow solution, from which it is re-precipitated unchanged on adding water. Although not a glucoside, it reduces Fehling's solution when heated with it; it also reduces silver nitrate and basic lead nitrate. Potas-

sium permanganate in alkaline solution and ferric chloride in alcoholic solution oxidise it to quinone. The action of nitric acid is characteristic; the concentrated acid has no action in the cold, but forms oxalic acid on heating; on boiling with very dilute (4 per cent.) acid, quinhydrone and quinone are successively formed. Its reactions place it in the class of oxyhydroquinones, since it gives as products of decomposition a di- or tri-hydroxybenzoic acid which colours ferric salts green, a polyvalent phenol, probably hydroxyquinol, and quinone. It is probable that two of the oxygen-atoms are contained in the same way as in hydroxycoumarin (umbelliferon).

Triacetylmoradin crystallises from its alcoholic solution in white, shining prisms which melt at 177—178°. It is not fluorescent, and has no acid properties. It is insoluble in alkalis in the cold, and decomposes when warmed with them.

Moradeïne crystallises in opaque, colourless prisms, very soluble in alcohol, ether, chloroform, &c., but only slightly in water. It melts at 199—200°, and exhibits the general reactions of an alkaloïd, forming a well-crystallised platinochloride and aurochloride, &c.

S. B. A. A.

True Winter Bark. (Drymis Winter-Forster.) By P. N. ARATA and F. CANZONERI (*Gazzetta*, **18**, 527—539).—After an historical summary of the introduction of the bark into Europe, the author describes the genuine bark from the Straits of Magellan; this occurs in the form of deeply-furrowed, curled-up fragments with an earthy fracture, exhibiting, when in small pieces, an internal reddish-brown coloration. When fresh, it has a bitter and pungent taste and an agreeable odour, recalling both turpentine and cloves. The sun-dried bark yielded: water (at 110°), 13·713 per cent.; ash, 3·338 per cent.; soluble in ether, 3·841 per cent.; in alcohol, 6·465 per cent.; in water, 13·981 per cent.; ligneous matter, 49·200 per cent. An analysis of the ash is also given. The ethereal solution contains a peculiar essence, fatty compounds, resins, and waxy matter; the alcoholic extract contains reddish, uncrystallisable resins. Citric acid was carefully looked for, but not found. The essence was isolated by distilling the bark with water, exhausting the distillate with petroleum, and distilling off the solvent. The crude oil, amounting to 0·0428 per cent. of the weight of the bark employed, is a mixture of several substances.

Winterene, $C_{15}H_{24}$, is the essential oil separated from this by fractional distillation. It passes over between 260° and 265°; sp. gr. at 13° = 0·93437. Index of refraction = 1·4931; sp. rotatory power at 16° $[\alpha]_j = +11·2$. It is readily oxidised on exposure to the air, becoming yellow. The formula $C_{25}H_{40}$ was calculated from the ultimate analysis and vapour-density, but the authors consider that the ready oxidisability of winterene and its analogy to similar essences points rather to the formula $C_{15}H_{24}$, which would place it in the group of sesquiterpenes, such as cedrene, cubebene, &c., the boiling points of which are between 250° and 268°.

Iodine dissolves in winterene producing a greenish-yellow coloration which changes to green after a time.

On adding picric acid containing a few drops of sulphuric acid to winterene, a yellowish-red, crystalline compound is formed.

Pure winterene is coloured green by a solution of bromine in chloroform, orange-red by a solution of chloral hydrate in sulphuric acid, rose to yellow by concentrated sulphuric acid or by sulphuric acid and chloroform, dirty-yellow by Fröhde's reagent and by ferric chloride and sulphuric acid, rose to violet by nitric acid.

The reactions of the essence after oxidation are also given.

S. B. A. A.

Nitrous Acid in the Atmosphere. By L. Ilosvay (*Bull. Soc. Chim.* [3], **2**, 666—667).—The liquid obtained by washing with water, bedewed grass and foliage-leaves, collected in the morning, contains nitrous acid, which is absent from noonday and evening gatherings. Nitrites are condensed on leaves during the day in damp, dull, rainless weather, and in dry, clear, sunny weather are replaced by nitric acid and ammonia.

Washed soils moistened and exposed to air determine similar surface condensations, the nitrogen-compounds being derived from the atmosphere and varying in amount with the duration of exposure.

T. G. N.

Causes of the Exhaustion of Arable Soil by Cropping without Manures. By P. P. Dehérain (*Ann. Agronom.*, **15**, 481—505).—The author has made a comparative study of certain plots at the experimental station of Grignon, some of which have been cropped without manuring for a number of years, while others have received regular dressings of farmyard manure.

Unmanured Plots.—Plots 21, 37, and 53 received no manure since 1874.

Manured Plots.—Plots 32, 33, 36, and 49 had received regular dressings of farmyard manure.

Comparative Crops. Sugar-beet.—In 1887 plot 37 yielded 13,900 kilos., and plot 53 10,000 kilos. per hectare, against 35,000—40,000 kilos. yielded by the regularly manured plots. *Red clover:* in 1888 plot 37 yielded 3,200 kilos. hay per hectare, and plot 53 2,600 kilos. against 8,800 kilos. yielded by a plot manured during the preceding years. *Trifolium incarnatum:* the continuously unmanured plot yielded 3,600 kilos. green in 1888 against 15,000 kilos. by the regularly manured plot. *Cereals:* for these crops the exhaustion is much less noticeable than for the preceding. In 1888, plot 37 yielded 31 metric quintals of oats (*avoine des salines*) against 33 by the manured plots; and plot 53 yielded 22 quintals of oats (*avoine à grappes*) against 32 yielded by the manured plots.

Although the difference is, in the case of the phosphoric acid, considerable, yet it cannot be said that the unmanured plots fail to yield crops on account of exhaustion of mineral food.

Phosphoric Acid and Potash in the Soil.

Percentage in the soil (depth not stated) of	Continuously unmanured.		Regularly manured.
	Plot 37.	Plot 53.	Plot 36.
Total P_2O_5	0·102	0·104	0·155
P_2O_5 soluble in acetic acid	0·012	0·015	0·034
Total K_2O soluble in aqua regia	0·090	0·091	0·117

Organic Matter in the Soil.—The carbon and nitrogen in the soils of plots 37 and 21 (unmanured) and of plots 32 and 49 (manured) were determined in 1878 and again in 1888 after 10 years' interval.

The results so far seem to connect the exhaustion, so conspicuous when beet-root or clover is grown, with the great loss of organic, and especially carbonaceous matter, the diminution in the important plant foods, nitrogen, phosphoric acid, and potash being relatively inconsiderable.

	Plots.		Plots.	
	37.	21.	49.	32.
Percentage of nitrogen in 1878	0·167	0·174	0·200	0·200
„ „ „ 1888	0·148	0·150	0·190	0·186
Loss	0·019	0·024	0·010	0·014
Percentage of carbon in 1878	1·519	1·630	1·52	1·66
„ „ „ 1888	0·730	0·730	1·61	1·60
Loss or gain	−0·789	−0·900	+0·09	−0·06
Proportion $\frac{C}{N}$ in 1878	9·0	9·3	7·6	8·3
„ „ „ 1888	4·9	4·8	8·4	8·5

The author next examines the various reasons that suggest themselves to account for this connection.

Retention of Moisture by Humus.—Parallel plots in the same strip of ground were selected from those continuously unmanured, and therefore poor in organic matter, and from those regularly or frequently manured and rich in organic matter, and samples taken carefully to the same depth and under exactly similar circumstances during every month from November, 1888, to November, 1889, for the determination of moisture. The results of each pair of plots are plotted in curves showing the percentage of moisture at the consecutive dates; but the

general results may be summed up thus:—The soil of the unmanured plots 21, 37, and 53, poor in organic matter, gave an average of 17·6 per cent. of water over the time named; that of the manured plots, 17, 33, and 49, rich in organic matter, 18·5 per cent. If this difference is reckoned on the hectare of soil, it amounts to 32·4 tons of water; but as the total water contained in the soil is 623·6—666 tons, no weight can be attached to the absence of so small a fraction. Other experiments showed that the difference in the loss by drainage was not greater than in the case of two samples of the same soil.

Quantity of Nitrates Formed.—Equal weights of the different soils were placed in glazed pots, and the initial nitrogen as nitrate determined in each. These pots were placed in the open, the drainage-water from each collected from May 14 to November 12, and the nitrogen as nitrate determined in each lot of water. The mean results for the plots in question were—

	Rain-fall.	Drainage.	Initial N as nitrate in soil.	N as nitrate in drainage.
	litres.	litres.	grams.	grams.
Plots 17 and 33 regularly manured ..	31·64	8·360	0·368	0·877
,, 21, 37, and 53 unmanured	31·64	9·116	0·322	0·624

From these figures it appears that the quantity of nitrate formed, even in the exhausted soils during the growing season, was amply sufficient for the requirements of good crops; 0·322 gram of nitrogen nitrified per 30 kilos. soil being equivalent to 113 kilos. per hectare.

Production of Carbonic Anhydride.—Determinations made by Boussingault and Lewy's method of the carbonic anhydride contained in 100 litres of the interstitial air of two soils on the same dates gave—

	June 7.	June 18.
	grams.	grams.
Plot 53 unmanured	1·13	0·98
,, 49 manured	1·38	1·16

These differences are again slight, and tend to confirm recent results of Wolny and of Schloesing, showing that there is no direct relation between the richness of a soil in organic matter and that of its interstitial air in carbonic anhydride. The foregoing experiments fail to yield any explanation of the facts, but the following one shows conclusively the actual importance of the organic matter of soil to the growth of sugar-beet. 30 kilos. of the rich soil of plot 49 and 30 kilos. of the exhausted soil of plot 53 were placed in similar pots, the latter being enriched by the addition of 3 grams of sodium nitrate, 3 grams of superphosphate, and 3 grams of potassium chloride, equivalent to 360 kilos. of each per hectare. Sugar-beet seeds were sown in each pot; on July 17 all the young plants but one were removed from each pot, and on October 25 the weight of the single root grown in each pot was taken.

	Soil rich in organic matter (49).	Soil artificially enriched (53).
	grams.	grams.
Weight of young plants removed July 17	6·78	2·51
,, entire plant on Oct. 25	730	165
,, root on Oct. 25	410	92
Percentage of sugar in juice	15·04	11·11
Sugar in entire plant	61·60	10·12

From all the facts given in this paper the author concludes that a portion of the organic matter of soil frequently manured with farm-yard manure probably serves as direct nutriment for the sugar-beet and some other plants, and that for this purely mineral food cannot be successfully substituted. J. M. H. M.

Experiments at Rothamsted on the Growth of Potatoes. By J. H. GILBERT (*Agr. Students' Gazette*, **4**, Pt. ii).—The experiments were conducted for 12 years on the same land. The following table shows the various manuring as well as the average yearly produce per acre for the 12 years, except in the farm-yard manure series, where the average of six years is given:—

	Good.		Small.		Diseased.		Total.	
	tons.	cwts.	tons.	cwts.	tons.	cwts.	tons.	cwts.
Unmanured	1	13·5	0	5·0	0	1·25	1	19·75
Superphosphate of lime	3	5·0	0	5·6	0	2·75	3	13·4
Mixed mineral manures	3	7·75	0	4·9	0	2·6	3	15 25
Ammonium salts	1	17·75	0	6·1	0	1·9	2	5·75
Sodium nitrate	2	4·6	0	5·25	0	2·6	2	12·5
Ammonium salts and mixed minerals	5	18·9	0	7·25	0	8·4	6	14·5
Sodium nitrate and mixed minerals	5	17·4	0	6·4	0	9 25	6	13·0
Farm-yard manure	4	11·9	0	7·0	0	5·75	5	4·6
Farm-yard manure and superphosphate	4	16·9	0	7·25	0	7·5	5	11·6
Farm-yard manure and superphosphate and sodium nitrate	5	17·75	0	6·6	0	17·9	7	2·25

The mixed minerals include superphosphate and potassium, sodium, and magnesium salts. The ammonium salts contained 86 lbs. of nitrogen whilst farm-yard manure supplied about 200 lbs. of nitrogen per acre per annum. It is remarkable that there is much less increase of produce of potatoes by nitrogenous manures alone than by mineral manures alone.

With regard to the various constituents of the tubers, the average amount of nitrogen per acre in those grown without manure was

only 14·9 lbs., which is less than would be yielded by wheat or barley grown under the same conditions. Mineral manures alone raised the amount of nitrogen to about 20 lbs., whilst nitrogenous manures alone only raised the amount taken up to 19·7 lbs. (with ammonium salts) and 23·0 lbs. (with nitrate). With the same application of nitrogen, but in conjunction with mixed minerals, the amount of nitrogen stored up in the tubers is raised to about 50 lbs. per acre. Of the other constituents, the most prominent is potash; under the influence of superphosphate alone, 30 lbs. per acre more potash is taken up than without manure, with superphosphate and mixed minerals (including potash) the increase is 33 lbs., whilst with minerals and nitrogenous manure together, nearly 70 lbs. more potash is recovered per acre than where no manure is applied. The presence of potash seems to be essential for the formation of starch and sugar. The accumulation of phosphoric acid, which is more directly connected with the nitrogenous constituents, is much less than that of potash.

As to the composition of the whole tubers and of the juice, there is an indication that the juice is richer in nitrogen, the more nitrogen there is applied in the manure and the less matured the crop; it includes, in fact, material for further maturation. The amount of juice is generally about 80 per cent. of the fresh tubers. The percentage of ash-constituents is higher in the juice than in the tubers; its amount varies considerably according to the manuring, but the composition of the ash of the tubers and the juice is always very similar. The greater part of the nitrogen is in the juice.

Of the total nitrogen of the tubers, Schulze found an average of 18·3 per cent. to exist as albuminoïds in the marc. In the Rothamsted experiments, the average was found to be only 15 per cent. The average percentage of total albuminoïd nitrogen was 56·2 (Schulze) and 63·6 (Rothamsted). The two sets of experiments show that, as a rule, less than 20 per cent. of the total nitrogen is in the form of insoluble albuminoïd. On the other hand, Schulze's results show an average of 43·8, and those obtained at Rothamsted 36·2 per cent. of total nitrogen, of the tubers to be non-albuminoïd: most of it existing as amides and much less as ammonia and nitric acid than is usual in the case of root crops. The nutritive value of this large proportion of nitrogenous matter is, to say the least, doubtful, and inasmuch as most of the albuminoïd matter itself is in the juice of the potato, it is probable that a good deal is lost as food.

Provided that the necessary minerals are present, the use of nitrogenous manure gives rise to a great increase of starch in the potato, just as in the case of root crops there is an increase of sugar under these conditions, and in the case of the cereals an increase of starch and cellulose. It is chiefly for the increased production of non-nitrogenous substances (starch, sugar, and cellulose) that direct nitrogenous manures are used.

Diseased potatoes contain considerably less dry matter than good ones, which is shown by the higher percentage of mineral matter in the dry substance of the bad ones to be due, not to acquisition of water, but to the loss of solid substance, and it is further shown that it is chiefly the non-nitrogenous organic substance which is lost. The

cause of the disease is a fungus which converts the starch into sugar; the loss of substance is perhaps mainly due to the evolution of carbonic anhydride, as a coincident of the growth of the fungus deriving its nutriment from ready-formed organic substance; a characteristic action in the growth of these non-chlorophyllous plants. The fungus accumulates a large proportion of both the mineral and nitrogenous substance of the juice of the tubers, which perhaps partly explains the fact that the disease develops much more in tubers grown by highly nitrogenous manures, and which have a highly nitrogenous juice, than in those grown under ordinary conditions. N. H. M.

Experiments with Farm-yard Manure. By E. HEIDEN (*Bied. Centr.*, **18**, 794—796; compare Abstr., 1888, 872).—The object of the experiments was to determine what changes take place when the liquid manure is kept alone, when treated with sulphuric acid containing phosphoric acid, and when kept covered with a layer of oil. The manure was well mixed, and three lots of 100 kilos. put into barrels and treated as described. Nitrogen as ammonia and organic nitrogen was determined in the manure at the beginning and at the end of the experiment, which lasted about six months. The manure kept without any preservative lost 11·9 per cent. of the nitrogen as ammonia and 18·5 per cent. of its organic nitrogen, corresponding with 12·9 per cent. of the total nitrogen. The sample treated with acid lost 13·8 per cent. of the ammoniacal nitrogen, but the amount of organic nitrogen was almost doubled, so that the loss of total nitrogen was only 1·5 per cent. The manure kept under oil lost 6·8 per cent. of the total nitrogen, or 5 per cent. of the ammoniacal nitrogen and 18 per cent. of the organic nitrogen. N. H. M.

Analytical Chemistry.

Modified "Orsat" Apparatus. By J. RUFFLE (*J. Soc. Chem. Ind.*, **8**, 3—4).—The author describes, with the aid of a diagram, a new form of bulb, which is said to be less subject to fracture and more easily prepared and cleaned than the bulb used in Orsat's apparatus for the rapid determination of oxygen. D. B.

Gas Sampling and Testing Apparatus. By J. E. STEAD (*J. Soc. Chem. Ind.*, **8**, 176—178).—The author describes, with the aid of a number of diagrams, various forms of apparatus for sampling and testing gases, designed by him for the purpose of examining blast and other furnace gases. The sampler is a modification of the apparatus described by Gruner, by which a large vessel filled with mercury is used to collect the gas. The author's apparatus is so arranged as not only to take the sample, but also to take the place of the old form of gas pipette. Three forms of gas-testing apparatus are described, their mode of working being explained with the help of diagrams. D. B.

The Concentration of Reagents. By R. Blochmann (*Ber.*, **23**, 31—35).—When the usual instructions for the preparation of reagents are carried out, the concentration of the solution obtained shows no relation whatever to that of an "equivalent" solution. It is, therefore, very difficult to estimate the amount of the reagent necessary in processes of precipitation, neutralisation, &c., and the author proposes, in order to overcome this difficulty, to make all the solutions approximately double-normal, normal, or semi-normal, according to the solubility of the substance; using the last-named strength for all expensive reagents. Very sparingly soluble salts, such as calcium sulphate, may be employed in saturated solutions, and the strength of oxidising and reducing solutions should be such that 1 litre will give off or absorb ($O/2 =$) 8 grams of oxygen. Under "concentrated acids" are understood anhydrous sulphuric acid, a saturated solution of hydrochloric acid, and a mixture of equal weights of anhydrous nitric acid and water. Tables giving the specific gravity and percentage composition of these solutions may be found in the original.

H. G. C.

Note by Abstractor.—A similar proposition to the above was made many years ago in Harcourt and Madan's "Exercises in Practical Chemistry," and the necessary directions for the preparation of the solutions may be found on p. 439 (3rd edition). H. G. C.

Estimation of Chlorine and Hydrogen Chloride in a Mixture of the two Gases. By W. Younger (*J. Soc. Chem. Ind.*, **8**, 88—90).—This method, which the author finds to give very accurate results, is based on the absorption of the gases in a standard solution of arsenious acid, to which a small quantity of sulphindigotic acid has been added. The absorption is accomplished in one vessel, described with the aid of a diagram, which, along with a graduated box as an aspirator, renders it possible to read off the grains of chlorine per cubic foot, the aspiration being stopped when the sulphindigotic acid is bleached. The hydrogen chloride may be estimated in the same solution by titration with silver nitrate. D. B.

Analysis of the Atmosphere. By O. Pettersson and A. Högland (*Ber.*, **22**, 3324—3325).—The authors find that the oxygen of the air may be accurately determined in the portable apparatus previously described (Abstr., 1887, 999), by means of absorption with a solution of sodium hyposulphite. The mean of very numerous determinations made in Stockholm during October, November, and the first half of December, 1889, gave the oxygen in the air as 20·940 per cent. L. T. T.

Estimation of Free Oxygen in Water. By M. Müller (*Chem. Zeit.*, **13**, 1188—1190).—The author comments on the uncertainty of the present methods for ascertaining the wholesomeness of water; he considers it desirable to inquire into the quality as well as the quantity of organic matter present, for which purpose oxidation with permanganate is not efficient, but the free oxygen in the water appears

to be an important factor. He has noticed in numerous experiments when waters have been retained in perfectly full, well-stoppered bottles, that in good waters the oxygen suffers only slight reduction or none at all, whereas in bad waters the oxygen is consumed with comparative rapidity in a few days, presumably on account of decomposing the readily oxidisable organic matter. It is pointed out that the free oxygen is not eliminated from water by boiling even for two hours. The author has devised the following method:—Some crystalline manganous sulphate is dissolved in the water, which completely fills a two- to three-litre bottle, fitted with a doubly bored india-rubber stopper, and connected by means of one bore with an upright wide tube filled with the same water; by lowering this, potassium hydroxide is admitted from the tap funnel in the other bore, causing the precipitation of manganous hydroxide, which absorbs all the free oxygen, forming manganic hydroxide. Hydrochloric acid and potassium iodide are now added through the funnel, the manganic oxide gives rise to the liberation of chlorine, which in its turn sets free iodine, the latter is titrated in a dish with sodium thiosulphate, and the amount of oxygen corresponding therewith is calculated. If nitrous acid is present, it is determined by adding hydrochloric acid and potassium iodide to a quantity of water equal to that taken for the oxygen estimation, titrating the liberated iodine, and deducting this quantity from the oxygen titration.

R. Hefelmann and K. Barth (*ibid.*, 1337) point out that this method is only applicable to waters free, or almost free, from organic matter, because organic matter not only absorbs iodine, but even chlorine, and also renders the direct estimation of nitrous acid impossible.

D. A. L.

Estimation of Sulphur in Pyrites. By G. LUNGE (*Zeit. ang. Chem.*, 1889, 473—477).—Objections have, on various grounds, been raised to the oxidation of the sulphur in pyrites by aqua regia, as advocated by the author. When barium sulphate is precipitated from a solution containing iron, low results are always obtained, in spite of the fact that the precipitate invariably contains iron. Jannasch and Richards have shown that this is due to the precipitation of a barium iron sulphate, which slowly loses sulphuric anhydride on ignition. When oxidising the pyrites in the dry way, Fresenius obtained about 1 per cent. more sulphur than by wet oxidation. In 1881 the author recommended as an improvement on his process that the iron should be removed by ammonia before precipitating with barium chloride. To this Jannasch and Richards objected that part of the sulphur would be contained in the precipitate as basic ferric sulphate. The author now shows that if the precipitation is performed according to the rules which he laid down in 1881, and which are embodied in the *Taschenbuch für Sodafabrikation*—"The warm solution to be mixed with a moderate excess of ammonia, filtered after 10 minutes, and the precipitate most thoroughly washed with boiling water"—the precipitate will not retain a trace of sulphate, and the results agree exactly with those obtained by dry oxidation. Results only about 0·2 per cent. lower can be obtained by the author's "old method" if the precipitate is only moderately

ignited, the errors compensating one another (compare Abstr., 1888, 85). Jannasch and Richards ignited their precipitate very intensely, and state that even after half an hour the expulsion of the sulphuric anhydride was not complete. The fusion method is less rapid than the aqua regia process, and is liable to the error of including in the estimation the sulphur in impurities (barytes, &c.), which is not available in practical use.

M. J. S.

Estimation and Occurrence of Sulphur in Coal. By G. H. BAILEY (*J. Soc. Chem. Ind.*, **8**, 360—365).—The author has examined the different methods in use for determining sulphur in coal. He finds that the magnesia method (Eschka's process) gives constant results, whilst the methods based on oxidation with potassium chlorate or potassium nitrate, and the methods due to Grace Calvert, show large variations between one determination and another. Experiments were also made with a view of learning what portion of the sulphur appeared in the flue gases, and what part remained in the ash, and whether these numbers were actually such as are arrived at by an examination of the coal according to the method suggested by Calvert. The results show that the sulphur existing in coal in the form of sulphates remains in the ash, and does not take part in the production of sulphurous anhydride in the flues. A large quantity of sulphur is also retained by the flue dust, and in samples examined by the author as much as 15 to 20 per cent. of sulphur has been found.

D. B.

Estimation of Sulphuric Anhydride in Fuming Sulphuric Acid. By B. SETLIK (*Chem. Zeit.*, **13**, 1670).—The following method is based on the fact that sulphuric acid only fumes so long as sulphuric anhydride is present. Water is run drop by drop from a graduated burette into 100 grams of the fuming sulphuric acid contained in a flask and well cooled. The operation is complete when a drop falling in the middle of the acid dissolves quietly without fumes; 1 c.c. of water corresponds with 4·444 per cent. of sulphuric anhydride. Acids containing above 35 per cent. of sulphuric anhydride should be diluted to 30—35 per cent. with monohydrated sulphuric acid of undoubted strength before titrating with water.

D. A. L.

Volumetric Estimation of Combined Sulphuric Acid. By L. W. ANDREWS (*Amer. Chem. J.*, **11**, 567—571).—The solution of the sulphate is diluted until it contains not more than 2 per cent. of sulphuric anhydride, and is then heated to boiling. Excess of a solution of pure barium chromate in hydrochloric acid is gradually added, and the boiling continued for a few minutes. Pure calcium carbonate now added to the hot liquid until no more carbonic anhydride is evolved, and the boiling again continued for a few minutes. The precipitate is filtered and washed until the wash-water is colourless, potassium iodide and hydrochloric acid are added to the filtrate, and the iodine liberated is titrated with a decinormal solution of sodium thiosulphate, 1 c.c. of which is equivalent to 0·002662 gram SO_3.

In the presence of ferric, nickel, or zinc salts, ammonia must be used instead of calcium carbonate to neutralise the acid liquid. The precipitate is, however, much more difficult to wash in this case, and a very thick filter must be used. The method is not available in the presence of phosphoric acid or of reducing agents. Test experiments are given, in which the error varies from 0·1 to 0·4 per cent. It is proposed to use this method for the indirect determination of sodium and potassium by weighing them as sulphates and estimating the sulphuric anhydride as described above. C. F. B.

Kjeldahl's Method of Estimating Nitrogen. By R. Niebling (*Chem. Zeit.*, 13, 1670—1671).—The author takes exception to the introduction of unnecessary complications in the distilling apparatus required for the Kjeldahl method. He points out that with a bulb in the distillation tube, into which perhaps the continuation of the tube may protrude, no soda passes over when the operation is conducted properly; moreover, with a tube sufficiently long ($\frac{1}{2}$ to 1 metre), even cooling may be dispensed with, the ammonia being completely absorbed if the tube only dips into the acid; such apparatus is readily rinsed and cleaned. To prevent bumping, zinc-dust is added to the alkaline liquid before distilling. The boiling should proceed slowly at the commencement. When measuring the acid with a pipette, the last drops are most uniformly removed, not by blowing, but by touching the side of the flask neck. D. A. L.

Estimation of Nitric Acid by Diphenylamine. By J. A. Muller (*Bull. Soc. Chim.* [3], 2, 670—672).—5 c.c. of a solution of diphenylamine (0·2 gram) in concentrated sulphuric acid (1 litre) is shaken with 1 c.c. of the clear liquid to be estimated, and the amount of nitric acid present is determined by a comparison of the blue tint produced with that yielded by solutions of potassium nitrate, corresponding to 0·5—5 milligrams of nitric anhydride per litre. The solutions to be estimated must not contain more than 0·01 gram of nitric anhydride per litre, or the colour produced is too deep for comparison.

The tint is not affected by dilute hydrochloric acid, but is altered by hydrobromic and hydriodic acids. T. G. N.

Detection of Traces of Nitrous Acid. By G. Lunge (*Zeit. ang. Chem.*, 1889, 666—667).—Ilosvay has improved Griess' test by using acetic acid instead of a mineral acid. The colour is more intense and more rapidly developed. He dissolves (1) 0·5 gram of sulphanilic acid in 150 c.c. of dilute acetic acid, (2) boils 0·1 gram of α-naphthylamine with 20 c.c. of water, pours off the colourless solution, and mixes it with 150 grams of dilute acetic acid. The author prefers to mix these two solutions, thus gaining the advantage of having only a single reagent instead of two, and one which indicates by its colour whether it has become contaminated by nitrous acid derived from the air. The mixture is not affected by light, but should be protected from the air. Should it, however, become coloured by absorption of nitrous acid, it may be shaken with zinc-

dust and filtered: the colourless filtrate is as serviceable as the original reagent. It will detect 1 part of nitrous acid in 1,000,000,000 parts of water. M. J. S.

Götz's Method of Estimating Phosphorus in Iron. By K. BORMANN (*Zeit. ang. Chem.*, 1889, 638—639; see Abstr., 1887, 865).—The author has improved the method, so that it is applicable to samples rich in carbon. 1·2 grams of steel is dissolved in 25 c.c. of nitric acid; the solution is concentrated as much as possible and treated with 8 to 16 drops of potassium permanganate solution containing 12 grams in a litre. The precipitated manganic peroxide is dissolved by a little hydrochloric acid, and the solution is again concentrated as much as possible. While hot it is mixed with 10 c.c. of a 25 per cent. solution of ammonium nitrate, and then 25 c.c. of Finkener's ammonium molybdate solution, and the whole is rinsed with ammonium nitrate solution into a pear-shaped vessel of 60—70 c.c. capacity, having at its smaller end a tubular prolongation of 40 mm. length, 0·2 c.c. capacity, and marked with 40 graduations. A number of these vessels are then rotated, at the same time, in a Braun's centrifugal machine for two minutes, whereupon the precipitate collects in the narrow tube, and its volume can be read off. Up to 0·25 per cent., silicon has no disturbing influence, but above that percentage gelatinous silica separates. A single estimation occupies half-an-hour, but 60 to 80 can be completed in four or five hours, and the results agree with gravimetric methods within $\pm$ 0·005 per cent. M. J. S.

The "Citrate Method" of Phosphoric Acid Estimation. By O. REITMAIR (*Zeit. ang. Chem.*, 1889, 702—709).—The author gives a copious review of the investigations and proposals that have been made in connection with this process, and then submits the following view of the nature of the reactions which take place:—The solution in ammonium citrate of the insoluble orthophosphates of the formula $M''HPO_4$ or $M''_3PO_4(M''_3 = M'''_2)$ results from the formation of soluble double salts of the constitution $M''NH_4PO_4,(NH_4)_3C_6H_5O_7$. When, however, M'' is magnesium, this double salt readily, but never quite completely, decomposes, with separation of $MgNH_4PO_4$, especially in presence of an excess of a magnesium salt. Now, on adding magnesia mixture to an ammoniacal solution containing phosphate and citrate, a small amount of this double salt is produced, together with magnesium ammonium phosphate and magnesium ammonium citrate, and, since the latter is incapable of decomposing the double salt, a portion of the phosphoric acid escapes precipitation. If, now, the original solution contains the double citrate of an earthy or alkaline earthy metal, the principal reaction consists in the conversion of this by magnesium ammonium citrate into the magnesium double salt, which is then, by a further quantity of magnesium chloride, decomposed as before, but when the excess of magnesium chloride is large, a small part of the original salt, $M''NH_4PO_4$, is precipitated, whilst if the excess of magnesium chloride is small, part of the magnesium double salt escapes decomposition. Moreover, if the amount of ammonium citrate is insufficient, the double earthy phospho-citrate

may be incompletely converted into $MgNH_4PO_4,(NH_4)_3C_6H_5O_7$, with the result that the precipitation will be slow and incomplete. Since the error caused by the imperfect decomposition of the magnesium ammonium phospho-citrate is fairly constant, its percentage amount may be reduced by taking a large quantity of substance; the quantity of ammonium citrate used must not be too small, but as the citrate is increased the quantity of magnesia mixture must be augmented also. The error caused by precipitation of $M''NH_4PO_4$ will be examined in a later communication. M. J. S.

Estimation of Water and Carbonic Acid in Salts. By T. M. CHATARD (*Amer. J. Sci.* [3], **37**, 468—471).—The author gives a drawing of an apparatus that has been used for the analysis of natural and artificial alkaline carbonates with very satisfactory results. About 1 gram of the salt is placed in a platinum boat, and inserted in a combustion-tube with a hot asbestos plug pushed in close behind the boat. The tube is connected with a U-tube containing glass beads moistened with sulphuric acid, and is gradually heated. A water-bath is now placed so that one limb of the U-tube, attached to the combustion-tube, fits into a curved recess in the side of the bath. A small spirit-lamp keeps the bath hot, so that the water driven out of the salt may not condense in the upper part of the limb. After highly heating the tube for half-an-hour, the water-bath is removed, and the apparatus allowed to cool. Throughout the process a current of perfectly dried air is passed through. As soon as the tube is cool, the U-tube is disconnected, and the boat, with its contents, removed, and placed in a weighed, well-stoppered glass tube. The increase of weight of the U-tube gives the amount of water in the sample, whilst the weight of the small tube subtracted from the sum of the weights of the tube, the boat, and the salt, shows a loss, which is water plus the carbonic anhydride originally existing as hydrogen alkali carbonate in the salt. It is found impracticable to collect and weigh the carbonic anhydride without sacrificing the water determination. The method is more rapid and quite as accurate as the distillation process. B. H. B.

Volumetric Estimation of Carbonates. By J. A. MULLER (*Bull. Soc. Chim.* [3], **2**, 483—485).—The coefficient of absorption per c.c. for carbonic anhydride in hydrochloric acid (containing 32 per cent. of hydrogen chloride) is 0·0018 gram per c.c., and in presence of quantities of calcium chloride, varying from 0·03—0·07 gram per c.c. is 0·0014 gram per c.c. T. G. N.

Estimation of Calcium in presence of Phosphoric Acid, Iron, Aluminium, and Manganese. By O. REITMAIR (*Zeit. ang. Chem.*, 1889, 357—362).—For the rapid estimation of calcium in such substances as basic slag, Immendorf precipitates it with ammonium oxalate in a solution feebly acidified with hydrochloric acid. The precipitate is free from phosphoric acid. It, however, contains small quantities of the other metals (as oxalates) and of silica, so that, whether the estimation is completed gravimetrically or by titration with perman-

ganate, the results are too high. The impurities can, for the most part, be removed by igniting the precipitate, dissolving in hydrochloric acid, oxidising with bromine, and precipitating with ammonia and ammonium sulphide. An abridged method consists in dissolving the impure calcium oxalate in hydrochloric acid without previous ignition, and reprecipitating by addition of ammonium oxalate and acetic acid, but the result is less exact. Still better is it to make both precipitations by Classen's method (Abstr., 1879, 969) with an intermediate ignition of the precipitate. The method is rapid, since filtration can be commenced a few minutes after precipitation, and the precipitates obtained are purer than by the other processes. The first is apt to contain somewhat considerable proportions of manganese, besides traces of other metals; the second is pure calcium oxalate. M. J. S.

Estimation of Zinc in Calamine. By W. Minor (*Chem. Zeit.*, **13**, 1670).—Ordinary calamine contains, besides zinc carbonate, varying amounts of zinc silicate and sulphide (blende). The total zinc is readily estimated in the usual manner; whilst the proportion of blende may be determined by boiling the calamine carefully with dilute sodium hydroxide, which dissolves the zinc carbonate and silicate, leaving the sulphide. The quantity of blende and zinc silicate together may be determined by boiling with 50 per cent. acetic acid, which removes the zinc carbonate. In this way the proportion of all three is ascertained.

Boiling with ammonia is of no use, as some, but never the whole of the zinc silicate, dissolves as well as the zinc carbonate. D. A. L.

Separation of Zinc from Nickel. By H. Alt and J. Schulze (*Ber.*, **22**, 3259—3262).—When hydrogen sulphide is passed into an aqueous solution of zinc sulphate and nickel nitrate, strongly acidified with succinic acid, the zinc is precipitated completely, whilst the whole of the nickel remains in solution; the solution may be hot or cold, and an excess of hydrogen sulphide has no effect on the results, but the precipitation must take place in absence of salts, otherwise nickel sulphide is precipitated. Quantitative experiments gave very accurate results.

The quantitative analysis of an alloy such as German silver, is best carried out as follows: The alloy (1·5 to 2 grams) is dissolved in nitric oxide, the solution freed from acid by evaporating, the stannic oxide separated by filtration, and the copper precipitated with hydrogen sulphide. The filtrate is evaporated to a small bulk to free it from hydrogen sulphide, almost neutralised with potash, heated to boiling, and treated with a 10 per cent. solution of sodium acetate (10 to 20 drops); the employment of a larger quantity of sodium acetate is unnecessary and disadvantageous. The basic ferric acetate is separated by filtration, the acetic acid expelled by boiling with a mineral acid, and the boiling solution treated with sodium carbonate. The precipitated zinc and nickel carbonates are washed, dissolved in succinic acid, the solution filtered to free it from threads of paper, and diluted to a known volume (500 c.c.). A portion

(100 c.c.) of this solution is mixed with succinic acid (5 grams), diluted with a little water, heated almost to boiling, and hydrogen sulphide passed in excess. The solution is kept for 24 hours to allow the precipitate to settle, then filtered, and the zinc sulphide washed in the usual way and weighed (as sulphide). The filtrate from the zinc sulphide is acidified with hydrochloric acid, evaporated to expel the hydrogen sulphide, heated to boiling, and the nickel precipitated with potash. Even in presence of a large quantity of succinic acid, the precipitation of the nickel is complete.

An analysis of German silver, carried out as described above, gave the following results (in percentages):—Sn = 0·08, Fe = 1·08, Cu = 63·25, Zn = 20·20, and Ni = 15·34, total 99·95 per cent.

F. S. K.

Application of Hydrogen Peroxide in Analysis. By C. Hiepe (*Chem. Zeit.*, **13**, 1303).—The author suggests the following expedient to avoid the inconvenience experienced by the separation of sulphur from the aqueous solution obtained by extracting the cold mass, after the fusion with sulphur and anhydrous sodium carbonate, in the analysis of alloys containing tin, antimony, copper, lead, bismuth, &c. The solution containing the tin and antimony is mixed with sodium hydroxide, heated to boiling, treated with hydrogen peroxide until colourless, avoiding excess, and a little hydrogen sulphide is then passed through the solution, or some sodium sulphide added to convert any heavy sulphates into sulphides. On acidifying this solution, tin and antimony sulphides are precipitated in a good condition to be readily washed or otherwise treated.

The hydrogen peroxide must be pure; the author has found magnesium chloride in many commercial samples.

D. A. L.

Precipitation of Manganese as Peroxide. By H. Alt (*Chem. Zeit.*, **13**, 1339).—When estimating manganese by precipitation with bromine, it is recommended to expel the air from the moderately acid solution, by boiling; to add ammonium chloride and ammonia, and then aspirate through it air previously passed through bromine-water; by this means the manganic hydroxide is precipitated without attaching itself to the sides of the containing vessel, and can be easily and perfectly transferred to a filter.

D. A. L.

Estimation of Iron in Water. By J. C. Bell (*J. Soc. Chem. Ind.*, **8**, 175).—70 c.c. of the water is evaporated to dryness in a platinum dish and the residue ignited gently. 1 c.c. of pure nitric acid is added, and the mass heated on a water-bath. The residue is again moistened with 1 c.c. of a 10 per cent. solution of hydrochloric acid, after which 5 or 10 c.c. of water is added, and the whole warmed on a water bath. The solution is then filtered, and made up to 50 c.c. in a 50 c.c. Nessler tube. The contents are transferred to another tube containing 1 c.c. of freshly prepared ferrocyanide solution, and treated with 1 c.c. of dilute nitric acid. This is then compared with a tube containing a known quantity of iron (see Abstr., 1875, 285).

D. B.

Estimation of Ferric Oxide and Alumina in Phosphatic Manures. By E. GLASER (*Zeit. ang. Chem.*, 1889, 636—638).—In the so-called "conventional method," in which the iron and alumina are separated from the calcium as phosphates by acetic acid, the results vary much according to the quantity of acetic acid used. The author has therefore sought to separate the calcium first, in order that the iron and aluminium phosphates may be thrown down by ammonia. The phosphate is dissolved in the usual way; 100 c.c. of the solution corresponding with 1 gram of the substance is placed in a $\frac{1}{4}$-litre flask, and mixed with 25 c.c. of concentrated sulphuric acid. After five minutes, alcohol is added and the mixture cooled, then made up to the mark and mixed. After half an hour it is filtered; 100 c.c. is evaporated in a platinum basin, and when free from alcohol is precipitated hot with ammonia, the excess of which is boiled off. After cooling, the precipitate is filtered off, washed with warm water, and ignited. Its weight, divided by 2, gives the joint amount of the bases. Numerous test analyses show the accuracy of the method, as well as the low results yielded by the "conventional method."

M. J. S.

Precipitation of Alumina and Ferric Oxide by Ammonia. By G. LUNGE (*Zeit. ang. Chem.*, 1889, 634—635).—If the older practice is followed of boiling off all the excess of ammonia, the precipitate will contain much basic sulphate, which will require prolonged ignition with the blowpipe to reduce it to oxide. In the author's improved method for estimating the sulphur in pyrites (p. 413) the precipitation of basic sulphates is avoided, but it remained to be seen whether the determination of the alumina was in any way affected by the free ammonia, and more especially whether accurate results would be obtained without the intense ignition. Four quantities of aluminium sulphate were acidified with hydrochloric acid, and then mixed with a moderate excess of ammonia. Three of them were filtered without boiling; of these, two were ignited with the blowpipe, and the third with a Muencke burner only. The fourth was boiled until almost all the ammonia was expelled, and the precipitate was ignited first with the Muencke burner and then with the blowpipe. The ultimate results of all four agreed closely, but the fourth only after intense ignition. This shows that (in presence of ammonium chloride) the excess of ammonia need not be boiled out, and that the precipitate then requires only moderate ignition (compare Meineke, Abstr., 1889, 441).

M. J. S.

Estimating Tungsten in Metallic Tungsten. By A. ZIEGLER (*Chem. Zeit.*, **13**, 1060).—In order to expedite the roasting for Preusser's method, the pulverised metal is mixed with dry ammonium nitrate; the roasting may then be conducted in a platinum crucible without fear of forming a platinum-tunsten alloy, inasmuch as the particles of tungsten become coated with oxide during the volatilisation of the ammonium nitrate.

D. A. L.

Analysis of Wolframite and Scheelite. By B. SETLIK (*Chem. Zeit.*, **13**, 1474). The wolframite or scheelite is finely pulverised and

dried at 110°; 3 to 5 grams are fused in a platinum crucible for about 2 hours with three or four times as much sodium carbonate. The mass is boiled with water, filtered, and washed. The iron and manganese may be estimated in the residue. For the estimation of the silica, tin, and tungsten, the solution is poured into excess of hydrochloric acid, boiled for half an hour, and the precipitate washed, dried, ignited, and weighed. The silica is then driven off by means of hydrofluoric acid, and the residue after weighing is fused with potassium cyanide until reaction ceases, extracted with water, and the metallic tin dissolved in iron sulphate and titrated with permanganate. The quantity of tungsten is then readily calculated. The amount of tungstic acid in wolframite varies from 60—80 per cent., and of manganese from 10 to 20 per cent. D. A. L.

Electrolytic Estimation of Antimony. By A. LECRENIER (*Chem. Zeit.*, 13, 1219).—Classen's method is efficient in the absence of polysulphides, but the removal of excess of sulphur entails much loss of time. The following modification is recommended:—The antimonous or antimonic solution is treated with excess of sodium sulphide, then with a 20 per cent. solution of sodium sulphite, and is carefully heated until colourless. When this solution is submitted to electrolysis, the antimony is precipitated in a few hours, and is free from sulphur. A current liberating 2·5 c.c. of water-gas per minute is the best, although a stronger current may be used. Some sulphur is deposited on the positive pole. D. A. L.

Separation of Bismuth from Lead. By G. LEMME (*Chem. Centr.*, 1889, ii, 939—940).—The author recommends Hertzog's method (*Chem. Centr.*, 1887, 1241); sufficient water must, however, be added to completely decompose the bismuth chloride, as also a sufficiency for the complete solution of the plumbic chloride; whilst, on the other hand, a sufficient amount of acid must be employed in order to prevent the precipitation of the oxychloride.

For the quantitative determination of lead in solution, the author has successfully employed the alkalimetric method, phenolphthalein being used as indicator. To the neutral solution of lead nitrate sufficient cold saturated solution of Rochelle salt is added to redissolve the precipitate at first formed; the solution is then coloured with phenolphthaleïn, and titrated with decinormal alkali until a deep-red coloration is produced. Finally decinormal nitric acid is added until decolorisation is produced. J. W. L.

Clarke's Soap Test. By F. L. TEED (*J. Soc. Chem. Ind.*, 8, 256).—The author finds that an equivalent of lime requires $1\frac{1}{3}$ equivalents of soap, or $CaSO_4$ requires $2\frac{2}{3}NaC_{18}H_{33}O_2$; whilst an equivalent of magnesia requires $1\frac{1}{2}$ equivalents of soap, or $MgSO_4$ requires $3NaC_{18}H_{33}O_2$. D. B.

Detection of Ceresin, Ozokerit, and Paraffin in Beeswax. By H. HAGER (*Chem. Centr.*, 1889, ii, 815—816; from *Pharm.*

Centralb., **30**, 565—566).—The specific gravity is determined by dropping the dried melted wax on to well sized paper, and submitting this to the swimming test described by the author (*Analyst*, **4**, 206). The density of pure wax he finds to vary between 0·956 and 0·964.

The test he recommends for paraffins is as follows: 1—2 grams of wax, finely cut up and dried by exposure to the air, is heated by a small flame until vapours commence to be evolved. A wide-mouthed vessel of one-half to two-thirds litre capacity is inverted over it, and the vapours allowed to condense. The first vapours collected are principally paraffin. The condensed substance is dissolved off with about 3 c.c. of chloroform, one-half of which is distilled off, and the residue saponified with a little sodium hydroxide. On cooling, the paraffin that may be present will swim on the surface. If a drop of the chloroform solution of the vaporised substance is allowed to evaporate on a glass slide, paraffin appears in the microscopical field in single fragments, which appear, when viewed with a low power, as stars. Vapour of pure beeswax is not so white as that of paraffin, and the chloroform solution of the deposit is dark coloured; whilst the residue of a drop deposited on the glass slide appears as a dull layer without stars. J. W. L.

Adulteration of French Essence of Turpentine. By A. AIGNAN (*Compt. rend.*, **109**, 944—946).—Essence of turpentine is frequently adulterated with about 5 per cent. of resin oil which cannot be satisfactorily detected by chemical methods. The resin oils are generally met with under three types: *selected rectified white oil*, $[\alpha]_D = -72°$, *best rectified white oil*, $[\alpha]_D = -32°$, and *rectified white oil*, $[\alpha]_D = -21°$. The first is generally used for the adulteration of the turpentine, and although it has a higher rotatory power of the same sign, the rotatory power of the mixture is lower than the normal rotatory power of the turpentine, $[\alpha]_D = -61° 30'$, which is practically constant for the pure essence from different sources. The rotatory power of the adulterated turpentine is measured, and the formula $[\alpha]_D = -61° 30' \frac{7° 30'}{5} h$ enables the percentage amount of the white oil h to be calculated. For adulteration with best rectified white oil, the expression is $[\alpha]_D = -61° 30' + \frac{8° 30'}{5} h$, and for rectified white oil $[\alpha]_D = -61° 30' + \frac{9° 30'}{5} h$. Sometimes essence of turpentine is mixed with *essence of resin*, the first product of the destructive distillation of resin, but this is detected by its strong disagreeable odour. The percentage proportion e can be calculated from the rotatory power by means of the formula $[\alpha]_D = -61° 30' + \frac{6}{5} e$ for ordinary essence of resin, and $[\alpha]_D = -61° 30' + \frac{3}{5} e$ for refined essence of resin. C. H. B.

Analysis of Essential Oils. By R. Benedikt and A. Grüssner (*Chem. Zeit.*, **13**, 1087—1088).—The authors have applied their method of boiling with hydriodic acid in the apparatus they devised, and have ascertained the "methyl number" (the quantity of methyl in 1 gram of the oil calculated from the weight of silver iodide obtained) in 57 samples of essential oils, in which the "acid," "ether," "saponification," and "iodine" numbers had previously been determined by Kremel. The "methyl number" for absolute alcohol is 326. A good many of the oils containing no methyl nucleus gave no "methyl number," such as oleum absinthii, amygdalar. amar., terebinthinæ, &c. For the others, the "methyl numbers" given are as follows; their origin is also given in the original paper:—

Ol. anisi	82·8
,, ,, *stellati*	79·8
,, *aurantii florum*	0·0
,, ,, *corticum*	6·9
,, *bergamottæ*	6·6 and 0
,, *betulini*	22·4
,, *calami*	24·2
,, *carvi*	6·6, 8·3, 0
,, *caryophyllorum*	88·8, 86·9, 73·8
,, *cassiæ florum*	6·7
,, ,, *foliorum*	73·2
,, *cinnamoni*	25·7
,, *citri cuticum*	23·6 and 0
,, *elemi*	12·1
,, *fœniculi*	65·7
,, *gaultheriæ* (artficial)	89·4
,, *laurocerasi*	13·8 and 0
,, *lavandulæ*	2·4 and 0
,, *olibani*	9·1
,, *petroselini*	92·2

The authors consider that these numbers will be useful in the examination of essential oils, and that the method should take its place among the quantitative reactions. The quantity of eugenol, anethoïl, &c., can be calculated from the "methyl number." Oils containing sulphur cannot be examined in this way; and those containing the higher alkyls, butyl, amyl, &c., may be known by not giving clear distillates over the silver iodide.

D. A. L.

Examination of Oil of Cassia. By H. Gilbert (*Chem. Zeit.*, **13**, 1406—1407).—It is pointed out that oils of cassia and cinnamon may be highly adulterated with resin oils and still pass the tests of the German Pharmacopœia. With nitric acid, sp. gr. 1·45 at 15°, or with 1·50 acid at 6°, both the pure and impure oils give crystals without development of heat; however, with the 1·50 acid at 15° both react violently, with development of heat and without the formation of crystals; therefore, the G. P. test, as neither the sp. gr. nor the temperature of the acid is stated, may lead to the condemnation of a pure oil

and *vice versâ*. By determining the "acid number," the adulteration can be detected, as the following numbers show:—

	Acid numbers.
Genuine oil of cassia (with 6 per cent. non-volatile residue)	13
Genuine oil of cassia after 40 hours' aëration	13
Genuine Ceylon oil of cinnamon (2 per cent. residue)	9
" " " " ($2\frac{1}{2}$ " ")	10
Adulterated oil of cassia (28 per cent. residue)	47
" " " (prepared from pure oil of cassia by intermixing 20 per cent. of colophony).	40
Colophony, sp. gr. 1·08	150

D. A. L.

Gravimetric Estimation of Thiocyanates. By H. ALT (*Ber.*, **22**, 3258—3259).—The following method can be employed for the estimation of thiocyanates; it is based on the conversion of hydrogen thiocyanate into hydrogen cyanide and hydrogen sulphate by oxidising agents such as nitric acid.

The thiocyanate is dissolved in water, a little more than the calculated quantity of crystalline barium chloride added, and the solution strongly acidified with nitric acid. Barium sulphate gradually separates from the solution, and the precipitation can be hastened considerably by warming gently. The hydrogen cyanide is then expelled by boiling, the solution is diluted with hot water, filtered, and the residual barium sulphate dried and weighed.

Quantitative experiments gave results agreeing very well with those obtained by Volhard's method. F. S. K.

New Reaction of Thiocyanic Acid. By G. COLASANTI (*Gazzetta*, **18**, 397—399).—Solutions of thiocyanic acid or of potassium or sodium thiocyanate acquire a permanent, bright emerald-green coloration on the addition of one or two drops of a solution of copper sulphate. The intensity of the coloration varies with the amount of thiocyanic acid present, which may be colorimetrically determined, therefore, by comparison with a standard solution. Although copper sulphate is a less sensitive reagent than ferric chloride, it is capable of imparting a green coloration to an aqueous solution containing $\frac{1}{4000}$ part of potassium or sodium thiocyanate.

The presence of thiocyanates in human urine may be well shown by preparing it in the manner indicated by Gscheidlen (Abstr., 1877, 205), and adding one or two drops of a dilute copper sulphate solution to the neutral aqueous extract. The intensity of the coloration obtained corresponds with a higher percentage of thiocyanic acid than that found by Gscheidlen.

Saliva must be freed from mucus by precipitation with alcohol, the filtrate evaporated to dryness on the water-bath, and the residue taken up with water and acidified with a trace of acetic acid before the addition of the copper sulphate. The green coloration is not so brilliant as that obtained with urine. S. B. A. A.

Examination of Crude Phenol and Cresol. By W. W. Staveley (*Chem. Zeit.*, **13**, 1126—1127).—It is pointed out that the method of testing crude phenols and cresols, by shaking with a double volume of 9 per cent. soda, and measuring the volume of undissolved liquid either with or without the addition of light petroleum, is untrustworthy, because, firstly, the quantity of soda is insufficient for material containing more than 60 per cent. of phenol; secondly, cresol, although insoluble in petroleum in the presence of water, is soluble when the petroleum contains 10—20 per cent. of coal-tar oils, moreover the higher homologues of cresol are soluble in any case; thirdly, the water in the crude phenol is taken up by the alkali, and is reckoned as phenol; and, fourthly, material containing even 2 to 3 per cent. of naphthalene gives a perfectly clear solution. The method is more workable if four volumes of 10 per cent. soda are used, the alkaline layer separated, neutralised with dilute acid, agitated with a measured volume of benzene, and the volume read off. In Williams' method for examining carbolic powders (this vol., p. 300), the quantity of alkali is also insufficient for treating rich material, whilst in Tidy's method not only is this the case, but also the solubility of the coal-tar acids in sodium sulphate is overlooked, and there is loss by volatilisation of the phenol. In Tóth's method the strong alkali, of sp. gr. 1·250—1·300, gives rise to a strong solution of the cresoxides, which dissolve large quantities of hydrocarbons; moreover any light hydrocarbons present could hold the free phenols in suspension, and so prevent their solution in the alkali. For estimating water in crude phenols, agitation of 50 c.c. with 30 to 50 c.c. of benzene and 30 c.c. of 50 per cent. sulphuric acid is recommended; the sulphuric acid is better than calcium chloride, which in its turn is better than sodium chloride. D. A. L.

Estimation of Glycerol in Soap Lyes and Crude Glycerol. By O. Hehner (*J. Soc. Chem. Ind.*, **8**, 4—9).—The author has investigated the chief methods in use for the estimation of glycerol in order to test their accuracy. He finds that the method based on the extraction of glycerol from the concentrated liquors by means of alcohol and ether is useless, unless the final evaporation is conducted in a vacuum, owing to the loss of glycerol by volatilisation. The lead oxide process gives good results with glycerols of fair purity, but in samples containing notable quantities of free alkali, sulphates, or resinous substances, the method gives untrustworthy results. The dichromate method is rapid, accurate, and presents no difficulty. With pure glycerol the oxidation is absolutely quantitative. Crude glycerols are treated as follows:—For the removal of chlorine and of aldehydic compounds, some silver oxide is added to a weighed quantity of the sample (about 1·5 grams), which is placed in a 100 c.c. flask. After slight dilution, the sample is allowed to remain with the silver oxide for about 10 minutes. Basic lead acetate is then added in slight excess, the bulk of the mixture made up to 100 c.c., and a portion filtered through a dry filter. 25 c.c. is placed in a beaker, and treated with 40—50 c.c. of standard dichromate solution, and about 15 c.c. of strong sulphuric acid; the beaker is then covered

with a watch-glass, and heated for two hours in boiling water. After this, the excess of dichromate is titrated back with ferrous ammonium sulphate.

The acetin method (Abstr., 1888, 1345) is rapid and simple, and gives concordant results when the following precautions are observed:—The heating at the various stages should be carried on in a reflux apparatus, and the sodium acetate should be cautiously heated before use. After acetylation is complete, the operations should be conducted as rapidly as possible, owing to the fact that triacetin is gradually decomposed when in contact with water. The free acetic acid must be neutralised as cautiously as possible, and with rapid agitation of the diluted solution, so that the alkali may not be locally in excess more than is unavoidable, on account of its action on the triacetin. To ensure the greatest amount of accuracy, the author advises taking the mean of the results obtained by the dichromate and triacetin methods. D. B.

Estimation of Glycerol in Wine and Beer. By H. v. Toerring (*Zeit. ang. Chem.*, 1889, 362—365).—The chief improvement introduced into the process is the purification of the glycerol by distillation under reduced pressure. The beer (50 c.c.) or wine (15 c.c.) is concentrated on the water-bath to 10 c.c., and then mixed with 15 grams of plaster of Paris. The resulting dry mass is powdered and extracted in a syphon extraction apparatus with absolute alcohol for six hours. The alcoholic extract, or the original wine, if it contained less than 5 per cent. of extractive matter, is mixed with a little water, and then evaporated until every trace of alcohol is expelled. The residue is introduced into a small retort (100 c.c.), enclosed in a sheet-iron air-bath, and connected with a Liebig's condenser, a flask to receive the distillate, and a pump. The water is first distilled over by heating the bath to 150—170° without working the pump. The apparatus is then exhausted to the tension of aqueous vapour, and the bath raised to 190—210°, when the glycerol distils over completely within an hour. After cooling, a little water is introduced into the retort and distilled over, to rinse out the last traces of glycerol. The distillate is best treated by the method of Diez. The aqueous solution, which should contain 0·5 to 1 per cent. of glycerol, is mixed with 5 c.c. of benzoic chloride and 35 c.c. of 10 per cent. soda solution, and is vigorously shaken for some time, with frequent cooling. When the precipitated glyceryl benzoate has hardened, it is crushed beneath the liquid, and collected on a tared filter, washed with water, dried at 100°, and weighed; 1 part of glycerol gives 3·85 parts of benzoate. M. J. S.

Polariscopic Estimation of Sugar in Sweet Wines. By A. Bornträger (*Zeit. ang. Chem.*, 1889, 477—486, 505—508, 538—545).—The sugar in wine is a variable mixture of dextrose and lævulose, with sometimes saccharose. The usual mode of examination consists in estimating the total quantity of sugar by titration with copper solution, and then ascertaining by the optical method the proportions of the two glucoses, and inverting with hydrochloric

acid for the detection of saccharose. The author considers that in our present ignorance of the true rotatory power and reducing action of lævulose, the exact calculation of the proportions of the sugars has only a relative value. His mode of preparing the wine for examination is as follows:—The wine is accurately neutralised in the cold with soda or potash, evaporated on the water-bath until the alcohol is expelled, mixed after cooling with a moderate quantity of lead acetate, made up to the original volume, and filtered. After the lapse of 24 hours this filtrate is fit for both polariscopic examination and for titration. If, however, the wine is so dark coloured that the above method only gives a sufficiently colourless filtrate when the amount of acetate is large enough to produce an alkaline reaction, it is necessary to neutralise the filtrate with acetic acid and dilute to double the volume. Special experiments have been made on each feature of the above process. Although the specific rotatory power of both dextrose and lævulose varies with the strength of the solution, yet within the limits occurring in wines the variations need not be taken into account. The specific rotatory power of lævulose increases, however, so much more rapidly than that of dextrose, that in wines containing a great excess of the former little more can be done than to state the fact of an excess. The removal of the alcohol is considered to be essential, since the specific lævorotatory power of inverted sugar diminishes with progressive increase in the amount of alcohol present; moreover, after removing the alcohol, less lead acetate is required for decolorisation. The evaporation temporarily reduces the rotatory power, but the original rotation is always restored by 24 hours' repose after dilution. The presence of alkaline chlorides (derived from the hydrochloric acid used for inversion and the alkali for subsequent neutralisation) increases the rotation, but with the proportions recommended (one-tenth vol. of acid of 1·1 sp. gr.), this is almost exactly compensated by the evaporation, for in the presence of chlorides the recovery of the rotatory power, diminished by evaporation, is not complete in 24 hours. It is very important to avoid an alkaline reaction at any stage, as even in the cold this soon diminishes the rotation. M. J. S.

Detection of Sugar in Urine. By WERNER (*Chem. Centr.*, 1889, ii, 812—813; from *Pharm. Centralh.*, **30**, 515).—The author has found that Maschke's modification of Böttger's test for sugar in urine always gives trustworthy results (this Journal, 1877, ii, 930).

J. W. L.

Unfermentable Dextrorotatory Constituent of Honey. By E. v RAUMER (*Zeit. ang. Chem.*, 1889, 607—609).—See this vol., p. 356.

Estimation of Potassium Hydrogen Tartrate and of Tartaric and Malic Acids in Wine. By R. GANS (*Zeit. ang. Chem.*, 1889, 669—671).—The investigation was undertaken to ascertain how far the estimation of these three acid substances by Borgmann's method would be affected by the presence or absence of other constituents of grape must and wine. The method consists in evaporating to a syrup,

precipitating the potassium hydrogen tartrate by alcohol and filtering, the precipitate being then dissolved in hot water and titrated by soda. The alcoholic filtrate is divided into two equal parts, one of which is neutralised with potash and then added to the other. The potassium hydrogen tartrate so produced is then separated as before, and the potassium hydrogen malate should be found in the filtrate. In presence of much sugar, a portion of the potassium hydrogen tartrate escapes precipitation, whilst, on the other hand, part of the tartaric acid is retained by the filter in spite of repeated washings with alcohol. This affects also the tartaric acid estimation, which is further vitiated by a portion of the malic acid not passing into the alcoholic filtrate. In the absence of sugar, however, nearly the whole of the malate is precipitated and is thereby estimated as tartaric acid, and at the same time the amounts of the other errors are altered. The method is therefore perfectly useless for comparing the acid constituents of must with those of the wine made from it. M. J. S.

Estimation of Tartaric Acid in Vinegar. By A. JOLLES (*Chem. Centr.*, 1889, ii, 944; from *Zeit. Nahr. Hygiene*, **3**, 185—186). —The author takes advantage of the fact that tartaric acid gives a yellow coloration with dilute ferric chloride solution. 5 c.c. of the vinegar is diluted to 1000 c.c., and of this solution from 5 to 20 c.c. is filled into narrow tubes so that the depth of liquid may be about 20 cm. 2 c.c. of the ferric chloride solution (1 per cent.) is added, and the depth of colour produced compared with that from known quantities of tartaric acid contained in similar tubes. For this purpose, a 0·1 per cent. tartaric acid solution is recommended. Coloured vinegars must be decolorised. J. W. L.

Adulteration of Milk. By PERRON (*J. Pharm.* [5], **21**, 63—66).— Samples of milk were suspected to be adulterated by the addition of fatty oil converted into an emulsion by means of borax or yolk of egg. In these cases the lactometer may give false indications. The borax is easily detected on examining the ash of the milk spectroscopically. The addition of oil to take the place of cream surreptitiously removed is readily ascertained by determining the solidifying point of the fatty acids obtained from the milk by evaporation, extraction with ether, saponification, and treatment with dilute sulphuric acid. Butter gives acids which solidify between 37·5° and 38·5°, whilst the oils give acids solidifying below 10°. J. T.

Testing Lard for Cotton-seed Oil and Beef Stearin. By J. PATTINSON (*J. Soc. Chem. Ind.*, 8, 30—32).—The silver nitrate test is based on the reducing action of cotton-seed oil, the reduced silver imparting a colour to the lard. The author recommends adding an alcoholic solution of silver nitrate to an ethereal solution of the lard. For beef stearin, the best test is the microscopical appearance of the crystals formed from an ethereal solution of the lard, the crystals of beef stearin forming curved tufts, the terminations being pointed and hair-like, whilst lard crystals are usually found in oblong plates, occasionally radiated, and have oblique terminations. The author

finds that pure lard has an iodine absorption of from 57 to 63, cotton-seed oil, 105 to 116, beef stearin, 23 to 28, and beef fat about 41 per cent. When the amount of cotton-seed oil is ascertained by the silver test, a near approach to the amount of beef stearin present can be calculated from the iodine absorption after making allowance for the influence of the known quantity of cotton-seed oil. The sp. gr. test is also useful. At 210° F., pure lard has a sp. gr. varying from 0·860 to 0·861, cotton-seed oil is 0·868, and beef stearin, 0·857. Some adulterated samples of lard which have come under the author's notice have had a sp. gr. of 0·8635. D. B.

Examination of Castor Oil. By H. GILBERT (*Chem. Zeit.*, **13**, 1428).—The test in the German pharmacopœia for castor oil cannot detect an admixture of resin oil, because the two kinds of oil have many properties in common; but saponification distinguishes between them: for example, an impure sample gave all the G. P. tests, and was right as to consistency and colour, but was suspicious in odour and taste; when saponified with soda, the number was 126 instead of 180—181·5, and the ether extract had the characters of resin oil. Moreover, when castor oil is shaken with an equal volume of nitric acid of sp. gr. 1·31, the former becomes slightly brown, the latter remains colourless, whereas the resin oil under similar circumstances becomes black and the acid yellowish-brown; whilst mixtures of castor and resin oils react like the latter, but with less vigour.

D. A. L.

Examination of Wax. By H. RÖTTGER (*Chem. Zeit.*, **13**, 1375—1376).—By Hübl's method, the wax is warmed with 95 per cent. alcohol and titrated with deminormal alcoholic potash, more alcoholic potash is then run in, the mass saponified by heating on a water-bath, and titrated back with deminormal hydrochloric acid; the first titration gives the "acid" number, the second the "ether" number, and the two together the "saponification" number.

Numerous investigations have shown that these numbers for pure yellow beeswax range respectively between 19 and 21 (mostly 20) for "acid" numbers, 73 and 76 (mostly 75) for the "ether" numbers, whilst the "saponification" numbers vary between 92 and 97, being in most cases 95, and the "ratio" of the "acid" to the "ether" numbers 1 : 3·6—3·8 (3·7).

Buchner examined some so-called pure, white wax, and from his results inferred that chemically bleached wax had higher "acid" and "saponification" numbers, 23·01 and 98·36, and a lower "ratio," 1 : 3·2. This has not been confirmed by subsequent investigators. Firstly, Helfenberg has shown that unpurified wax, or that purified either with charcoal or with permanganate, does not give abnormal numbers, and now the author has obtained the following numbers from wax bleached with sulphuric acid:—

Sp. gr.	"Acid" number.	"Ether" number.	"Saponification" number.	Ratio.
0·966	20·2	76·7	96·9	3·79

Therefore it does not appear necessary to adopt any different normal numbers for bleached than for yellow wax. The author points out that often the so-called genuine wax of commerce is no such thing; for example, two samples marked genuine and pure gave the following numbers:—

	I.	II.
"Acid" number..........	29·7	31·46
"Ether" "	87·5	67·66
"Saponification" number..	117·2	99·1
"Ratio"	2·9	2·14

D. A. L.

Analysis of Methylanilines. By F. REVERDIN and C. DE LA HARPE (*Bull. Soc. Chim.* [3], **2**, 482—483; compare Abstr., 1889, 1038; this vol., p. 309).—Replying to the criticism of Giraud on their process, the authors deny the necessity for employing absolutely pure acetic anhydride, and state that if the operation is conducted in a large cooled flask there is no need to dilute the reagent.

T. G. N.

Estimation of Nicotine in Tobacco. By R. KISSLING (*Chem. Zeit.*, **13**, 1030).—Popovici (Abstr., 1889, 802) obtained low results by the author's method when estimating nicotine by means of the polariscope, and he attributed it to loss by volatilisation while evaporating the ether. The author now states that when the operation is carefully conducted the loss from this source is negligible; moreover, as Popovici compared his tobacco extracts with standard numbers obtained with pure nicotine solutions, the author suggests that the results may be influenced by substances other than nicotine present in the tobacco extracts. D. A. L.

Estimation of Tannin by Permanganate. By F. GANTTER (*Zeit. ang. Chem.*, 1889, 577—580).—The method known as the "cubic centimetre method" gives results which vary much with comparatively small alterations in the manner of conducting it. Seemingly, the oxidation of both the tannin and the indigo used as indicator is very imperfect in the cold. At the boiling temperature the oxidation is complete, but the end of the reaction is masked by the formation of a brown precipitate. This can be dissolved by boiling with a known quantity of oxalic acid, and the titration can then be completed with the same ease as one of oxalic acid alone. From experiments with pure tannin, as well as from others with extract of oak bark, in which a gravimetric method was used for comparison, it is found that 1 milligram of tannin requires 3·988 milligrams of potassium permanganate (or is equivalent to 7·951 milligrams of oxalic acid), and that within wide limits the concentration of the solution has no influence. The solutions required are—(1) potassium permanganate, containing 3·988 grams per litre; (2) oxalic acid, 7·951 grams per litre. The extract from 10 grams of bark is made up to 1 litre; 10 c.c. is mixed with 10 c.c. of dilute sulphuric acid and heated to boiling. Permanganate is then added in quantities of 1 c.c. until the disappearance of the red colour becomes slow; the

mixture is again boiled up, and the permanganate is added drop by drop, waiting each time until the liquid has become colourless. When the brown precipitate no longer disappears on vigorous boiling, 1 c.c. more is added, and the boiling is continued for some time. Oxalic acid is then added until the liquid is colourless, and the titration is finished as usual. For accurate work, a second portion of the extract should be titrated in the same manner after removal of the tannin by hide, but for technical purposes this is scarcely necessary.

M. J. S.

Volumetric Estimation of Tannin in Wines. By L. Roos, Cusson, and Giraud (*J. Pharm.* [5], **21**, 59—63).—A 10 per cent. solution of tartaric acid is made very slightly alkaline by the addition of ammonia, and to this is added a neutral lead acetate solution until the precipitate which first forms just ceases to be redissolved; after being filtered, the solution is ready for use. This solution completely precipitates tannin from its solutions; it is standardised by means of a solution of pure tannin as follows:—25 c.c. of a tannin solution of 5 grams per litre is placed in a flask with 4 or 5 drops of ammonia. The lead aceto-tartrate solution is run in, a couple of c.c. at a time, from a burette. After each addition, a drop of the solution is placed on a double filter-paper, the upper one of which retains any precipitate that may have been conveyed by the drop, while a drop of sodium sulphide is brought into contact with the liquid in the lower paper. A brown stain, due to excess of lead, only appears after the tannin is completely precipitated. After a preliminary estimation, the titration is more accurately made by adding a few drops at a time of the lead solution when near the end of the process. The estimation of tannin in wine is made in precisely the same manner. The method is very rapid, and gives very satisfactory results. J. T.

Determination of Lupulin in Hops. By F. Reinitzer (*Bied. Centr.*, **18**, 859).—A portion of the hops (not weighed) is sifted by Haberlandt's process, and any grains which pass through the sieve removed with forceps. The lupulin is then weighed, shaken, and washed with chloroform into a dry filter, in which it is then wrapped and extracted with chloroform for about an hour. When dry, it is removed from the filter-paper to the weighing glass previously used, and weighed. The amount of lupulin husks is thus determined, and that of the lupulin found by subtracting this amount from the original weight.

A second weighed portion of the hops is then extracted with chloroform in a Soxhlet's apparatus, shaken on a sieve, the pieces of leaf removed with forceps, and the lupulin brushed through. The sifted portion is again sifted to obtain it free from grains. The pure lupulin husks are now weighed, and from the numbers, with the help of those previously obtained, the original weight of lupulin is calculated. The method gives much more concordant results than that originally employed by Haberlandt, and gives a better insight into the composition of hops than was previously possible. Examples of analyses are given which support this statement. N. H. M.

Diastasic Power of Extract of Malt. By R. A. Cripps (*Pharm. J. Trans.* [3], **20**, 481).—The author refers to the very discordant results of published determinations of the digestive power of malt extracts; he describes his slightly modified method of estimation, and declares that extract of malt should completely digest its own weight of potato starch in from 10 to 15 minutes at 37°. R. R.

Detection of Carbonic Oxide Hæmoglobin. By A. Welzel (*Chem. Centr.*, 1889, ii, 942; from *Centr. med. Wiss.*, **27**, 732—734). —Zinc chloride or very dilute platinic chloride solutions produce a bright-red coloration with carbonic oxide hæmoglobin, whilst normal blood is coloured brown or very dark brown. If the blood is diluted with water, the precipitated hæmatin and albumin are coloured. Carbonic oxide blood after standing in cold water for two minutes becomes raspberry-coloured, oxyhæmoglobin greyish-brown. 25 per cent. of carbonic oxide blood was detected by this means. Phosphomolybdic acid or 5 per cent. phenol produces a carmine-coloured precipitate with carbonic oxide blood, a reddish-brown one with oxyhæmoglobin; 16 per cent. of the former can be detected by this reaction. If 15 c.c. of 20 per cent. potassium ferrocyanide solution in 2 c.c. of dilute acetic acid is added to 10 c.c. of carbonic oxide blood, an intense, bright-red coloration is produced; normal blood becomes dark-brown-coloured with this treatment. If 4 parts of normal blood is diluted with 4 parts of water and shaken with 3 volumes of a 1 per cent. tannin solution, it becomes coloured primarily bright-red with a yellowish tinge; at the end of 1 to 2 hours it has become brownish, and finally has turned grey at the end of 24 hours; carbonic oxide blood treated in the same manner is also coloured bright-red at first with a bluish tinge, which colour, however, remains unchanged. Both of these reactions were observable with 1 per cent. carbonic oxide blood in 1·0 per cent. hæmoglobin, and carbonic oxide was detected in air by its means when present to the extent of 0·0023 per cent. Phenylhydrazine produces a bright-red coloration with blood containing carbonic oxide, and a dark-red coloration changing to black with normal blood; the blood is diluted to 1 in 40 for this reaction. If more than 5 drops of the phenylhydrazine solution is added, a greyish-violet coloration is obtained with oxyhæmoglobin, and a rose-red colour with carbonic oxide blood. A rabbit died when its blood was three-fourths saturated with carbonic oxide.

J. W. L.

General and Physical Chemistry.

Refractive Power of Solutions of Simple Salts. By E. DOUMER (*Compt. rend.*, **110**, 40—42).—If μ is the refractive power of the salt with respect to water, and Pm its molecular weight, then the product μPm is the *molecular refractive power*. All salts of the same acid and of the same type have the same molecular refractive power. For the chlorides $M'Cl$, $\mu Pm = 21·5$; for the chlorides $M''Cl_2$, 42·8; for the sulphates M'_2SO_4, 42·5; for the sulphates $M''SO_4$, 43·1; for the nitrates MNO_3, 21·7.

The molecular refractive powers of salts of different types are multiples of the same number—

KCl.	K_2SO_4.	Na_3PO_4.	$PtCl_4$.	$Al_2(SO_4)_3$.
20·7	43·1	64·3	89·8	130·5

The molecular refractive power is a function of the valency of the metallic constituent of the salt.

The observed deviations from the mean value of μPm may be traced to chemical as much as to physical causes. Seven out of the sixty-two salts examined seem to depart from the third law. Twenty examples of double salts indicate that their refractive power is the sum of the refractive power of their constituents.

These results lead to the conception of *optical equivalents*.

C. H. B.

Refractive Power of Solutions of Double Salts. By E. DOUMER (*Compt. rend.*, **110**, 139—141; see preceding abstract).—The molecular refractive power of double salts is the sum of the molecular refractive powers of their constituent salts, a result similar to that obtained by Berthelot and by Landolt with certain organic liquids.

The refractive power of different double salts is proportional to the valency of their respective metallic constituents. It follows that the refractive powers of any salts, double or simple, are proportional to the valencies of their metallic radicles. These facts make it possible to determine the refractive power of a simple salt which is difficult to prepare and purify alone, but which forms readily crystallisable double salts.

Observations of the refractive power also throw light on the constitution of double salts. For example, if potassium ferrocyanide is a compound of K_4 with the radicle FeC_6N_6, the sum of the valencies of the metal is 4, but if it is a double cyanide $4KCN,Fe(CN)_2$, the sum of the valencies of the metals is 6. As a matter of fact, the refractive power of the ferrocyanide is $21·5 \times 6$, and hence it would follow that it is really a double salt.

C. H. B.

Absorption of Ultra-Violet Rays by Derivatives of the Paraffins. By J. L. Soret and A. A. Rilliet (*Compt. rend.*, **110**, 137—139).—It is very difficult to obtain compounds sufficiently pure for observations of this kind. The alcohols show great transparency to the ultra-violet rays, and apparent exceptions are probably due to impurities. The rectification and prolonged desiccation of the alcohols often leads to slight oxidation, which greatly impairs their transparency. Hartley and Huntington concluded that in the series of alcohols the absorption of the ultra-violet increases as the complexity of the molecule increases. The authors found, however, that if the process of drying had been rapidly carried out, ethyl alcohol is not appreciably less transparent than methyl alcohol.

Ketones are very opaque to the ultra-violet rays, but the differences between different individuals were not greater than might be attributed to small quantities of impurities.

Haloïd-derivatives containing the same electro-negative radicle do not differ appreciably in their absorptive power, or, in other words, the substitution of one alkyl radicle for another has little effect on their transparency. This is especially well marked in the case of the iodo-derivatives. The haloïd salts of sodium and potassium are decidedly less opaque than corresponding alkyl-compounds, and, hence, the substitution of an alkyl radicle for an alkali metal reduces the transparency. There are other differences between the spectra of the two classes of compounds which indicate that their molecular grouping is not similar. Haloïd-derivatives containing different electro-negative radicles have very different degrees of transparency, iodo-derivatives absorbing most, and bromo-derivatives less, whilst chloro-derivatives are very transparent.

Pure ether is almost as transparent to ultra-violet rays as pure water.

No new conclusions were drawn from an examination of many acids of the acetic series and their sodium and alkyl salts. The difficulties in the way of obtaining these compounds sufficiently pure are extremely great. Vapours of liquids which are volatile and have sufficient absorptive power, also exert an absorptive action on the ultra-violet rays.

The action on the ultra-violet rays constitutes a very delicate test of the purity of an organic compound. C. H. B.

Spectroscopic Evidence of Traces of a New Element, belonging to the Eleventh Series in Mendeléeff's Table, and occurring in Tellurium and Antimony, and also in Copper. By A. Grünwald (*Monatsh.*, **10**, 829—861).—The author finds a coincidence between certain of the lines in the ultra-violet spectra of tellurium, antimony, and copper, and argues that this points to the occurrence of a common impurity in the three elements. He is of opinion that this impurity was originally present in the tellurium, and that from this a portion of it is transferred to the antimony and copper in the reduction of these metals from their ores. Many of the above coincident lines are transformed on multiplication by $\frac{11}{10}$ into lines of the primary element "*b*" in the water spectrum, and

this, in accordance with the principle formerly laid down by the author (Abstr., 1889, 455), indicates that the above impurity largely consists of an element occurring in the eleventh horizontal line in Mendeléeff's table. The character of the spectrum shows that it cannot be one of the known elements in this series, and the author believes that it is an unknown element in the tellurium group, with an approximate atomic weight of 212, and probably identical with Brauner's austriacum. It is, therefore, an element which in general properties closely resembles tellurium and also antimony, and is, hence, difficult to separate from these. In copper, it probably behaves as an electronegative element, on the assumption that pure copper is an alkali metal of low melting point, and is ordinarily found combined with this difficultly fusible non-metallic constituent.

The author states that Brauner, according to a verbal communication, has quite independently arrived at conclusions similar to the above. H. C.

New Fluorescences. By L. de Boisbaudran (*Compt. rend.*, **110**, 24—28 and 67—71).—The author has examined the fluorescences obtained with the oxides of samarium, $Z\alpha$, and $Z\beta$ as active substances, and silica, zirconia, stannic oxide, and tantalic oxide as solid solvents.

Samarium oxide in silica gives a moderately intense rose-red fluorescence with a spectrum of one very broad red band. If the passage of the discharge is continued, the rose-red fluorescence becomes feeble, and is partially replaced by the blue fluorescence of pure silica. The same mixture, previously more strongly heated, gives a fine orange fluorescence, showing three broad nebulous bands, each containing a very distinct although slightly nebulous line.

Samarium oxide in zirconia gives at first a beautiful orange fluorescence with several well-defined lines, but their brilliancy and distinctness rapidly diminish as the passage of the discharge continues.

$Z\alpha$ in silica gives a brilliant yellow fluorescence characterised by a strong dissymmetrical band. The fluorescence of $Z\beta$ was faintly visible, and as the discharge continues, the bands of $Z\alpha$ fade considerably but those of $Z\beta$ remain unaltered.

$Z\alpha$ (1 per cent.) in zirconia gives a yellow fluorescence which at first is somewhat brilliant, but rapidly becomes feeble as the discharge continues. The spectrum contains a yellow and a blue band, each with a nebulous line, and is very different from that of $Z\alpha$ in silica.

$Z\beta$ (0·42 per cent.) in silica gives a fluorescence which at first is brilliant and almost white, but quickly becomes green, because the yellow band of $Z\alpha$, present as impurity, fades rapidly, whilst the green band of $Z\beta$ retains its intensity. It follows that the fluorescence is a more sensitive test for $Z\alpha$ than for $Z\beta$, a result which is also obtained in other media.

$Z\beta$ (2 per cent.) in zirconia gives only a yellow fluorescence showing nothing but a feeble spectrum due to the presence of traces of $Z\alpha$.

Samarium oxide in stannic oxide, previously heated at the melting

point of silver, shows only a feeble orange fluorescence, but if more strongly calcined, it gives at first an orange-yellow to pale-yellow fluorescence, according to the perfection of the vacuum. This, however, very rapidly becomes faint as the passage of the discharge continues; and the same stannic oxide alone gives a yellow fluorescence which is very similar to that obtained in presence of samaria and is probably due to some impurity.

Samaria in tantalic oxide gives a dull orange fluorescence which becomes feebler as the discharge continues, although less rapidly than when zirconia or stannic oxide is the solvent. Its spectrum consists of two somewhat feeble, broad and nebulous bands, similar in position to those given by samaria in alumina, but different in character.

$Z\alpha$ (1 per cent.) in stannic oxide gives no noteworthy fluorescence.

$Z\alpha$ (1 per cent.) in tantalic oxide, after strong calcination, gives a very feeble greenish-yellow fluorescence which rapidly becomes fainter as the discharge continues. It shows faintly the bands due to $Z\beta$.

$Z\beta$ (3 per cent.) in stannic oxide also gives practically no fluorescence.

$Z\beta$ (3 per cent.) in tantalic oxide gives a beautiful but not very brilliant, slightly yellowish-green fluorescence which is less affected by the continuation of the discharge than the corresponding fluorescence of $Z\alpha$. The bands of $Z\alpha$ were also faintly visible.

These results afford further evidence of the fact that the fluorescence of one and the same active substance may vary considerably in different solvents. The alterations in the bands, &c., may be due to combination taking place between the solids. There is a general similarity between the spectra of the same substance in various media, but when it is a question of identity or otherwise between two substances, it is essential that the conditions should be identical. The rapid extinction of the fluorescence observed in some cases when the discharge is continued depends on both the nature of the active substance and the nature of the solvent. In silica or tantalic oxide, the fluorescence of $Z\alpha$ fades rapidly, but that of $Z\beta$ does not alter. The fluorescences of samarium oxide and $Z\alpha$ in zirconia fade more rapidly and completely than in silica. As a rule, the fading depends more on the solvent than on the active substance, but each constituent of the mixture tends to confer on it its own special properties.

Samaria in alumina and silica respectively affords a good example of the influence of calcination on the fluorescence. Samaria in alumina moderately calcined gives a spectrum of three diffuse bands, the central orange one having a relatively distinct line; but the same mixture, after being more strongly heated, gives a second spectrum of a totally different type, consisting of three groups of much more brilliant and distinct lines, their mean wave-lengths being higher than those of the bands of the first type. Samaria in silica, however, when treated similarly, gives only a spectrum of the first type, the three bands being much more luminous than in the case of alumina, and each having a strong line. Of course the position of the bands is not the same with the two oxides. C. H. B.

Conditions of Equilibrium between Electrolytes. By S. Arrhenius (*Zeit. physikal. Chem.*, 5, 1—22).—The author first considers the equilibrium between an acid and one of its salts. If x represents the fractional amount of dissociated acid, and d that of the salt, and V the volume in litres containing a gram-molecule of the acid, and n molecules of the salt, then $(nd + x)x = KV(1 - x)$, K being the dissociation constant which is determined from the conductivity of the acid. This formula is found to hold in the case of acetic and formic acids and their sodium salts. For feeble acids x is small, and in comparison with nd or 1 becomes negligible, so that since d is practically independent of the dilution, the degree of dissociation, that is, the strength of a feeble acid when a salt is present in the same solvent, becomes proportional to the amount of the salt.

Equilibrium between a feeble acid, such as acetic acid, and a salt such as sodium chloride is a case of equilibrium between four substances, the above two and the sodium acetate and hydrochloric acid that are formed. If the fractional dissociation of these substances in the order named be expressed by $d_1d_4d_2d_3$, and 1 mol. of acetic acid on being brought into contact with n mols. of NaCl gives rise to x mols. of HCl and sodium acetate, then—

$$d_2x \cdot d_3x = d_1(1 - x)d_4(n - x).$$

This expression is also found to agree with the experimental results.

From this last expression it is possible to deduce a value for the so-called "avidity" measured by Thomsen and Ostwald, and the author finds that for monobasic acids the avidities for any given dilution are approximately proportional to the degrees of dissociation of the acids at this dilution. Ostwald's results are shown to be in agreement with this conclusion.

It is found from the above that the Guldberg-Waage theory is only applicable to equilibrium between four electrolytes when two out of the four are strongly dissociated. The conclusion drawn from this theory, that the avidities of acids are proportional to the square roots of their affinity coefficients, is incorrect.

The decomposition of certain salts by water, which was observed by Walker to follow the ordinary laws of mass action, is shown by the author to take place in accordance with the equation last stated. In this case it is necessary to assume that the water is an electrolyte and partially dissociated. H. C.

Electrolytic Crystallisation and Dimorphism of Lead. By O. Lehmann (*Zeit. Kryst. Min.*, 17, 274—279).—The author has formerly shown that the electrolytic formation of crystals may be compared with ordinary crystallisation on the assumption that the metal which separates out at first remains dissolved in the electrolyte, and that, when the latter becomes saturated, it crystallises out in the ordinary manner. Ostwald has shown that the free metal may be capable of existing in the electrolyte (Abstr., 1888, 1142), and the above view is also supported by the observation of the author (this vol., p. 317) that during electrolysis, the metal which separates out is deposited more readily on an electrode of the like metal than on that

of another. He now finds that when the strength of the current is increased until the metal no longer forms a uniform deposit on the surface of the electrode, the crystals that are deposited arrange themselves into a skeleton-like structure, and that further increase in the current strength will only alter the mass of the structure, but not its form. Lead forms an apparent exception to this rule, for with a weak current it separates out in leafy crystals which appear to belong to the monosymmetric system, and are similar to those forming the ordinary lead tree; whilst with a strong current the crystals obtained are those of the regular system and under favourable circumstances, well formed octohedra.

To explain this dimorphism, the author assumes that the rate at which the lead-atoms separate out being far less in the first than in the second case, different molecules are formed in the solution, and that since, as above stated, the metal separates out from the solution in crystalline form, the one set of molecules will form crystals which are distinct from those of the other. H. C.

Sodium Phosphite and Pyrophosphite. By L. AMAT (*Compt. rend.*, **110**, 191—194).—*Disodium phosphite*, $HPO_3Na_2 + 5H_2O$, is neutral to phenolphthaleïn, and melts at 53°; heat of dissolution at 13·5 = − 4·6 Cals. The anhydrous salt is obtained by drying the preceding salt in a vacuum, and finally at 150°; heat of dissolution at 13·5° = + 9·15 Cals.

Monosodium phosphite, $2HPO_3HNa + 5H_2O$; heat of dissolution at 15° = − 5·3 × 2. Heat of dissolution of the anhydrous salt = + 0·75 Cal. at 13°, but increases distinctly with the temperature. Combining these numbers with the heat of solution and neutralisation of phosphorous acid, and the heat of dissolution of sodium hydroxide, we have—

PO_3H_3 solid + NaOH solid = HPO_3HNa solid + H_2O solid....................	develops	+25·2 Cals.
PO_3H_3 solid + 2NaOH solid = HPO_3Na_2 solid + $2H_2O$ solid..................	„	+41·6 „

Sodium pyrophosphite; heat of dissolution at 13° = + 0·3. If the pyrophosphite were at once transformed into phosphite in contact with water, it would be very considerably higher, and hence a solution of the pyrophosphite is not identical with a solution of the acid phosphite, a fact which is also proved by its behaviour with phenolphthaleïn, methyl orange, and silver nitrate.

The pyrophosphite is converted into phosphite or phosphorous acid by treatment with sodium hydroxide or sulphuric acid respectively. The change $H_2P_2O_5Na_2$ solid + H_2O liquid = $2HPO_3HNa$ solid develops + 2·54 × 2 Cals., according to the result with soda; whilst the results with sulphuric acid give $H_2P_2O_5Na_2$ solid + H_2O solid = $2HPO_3HNa$ solid develops + 6·23 Cals.

From the heat of dissolution of the monosodium phosphites, $2HPO_3HNa$ solid + $5H_2O$ solid = $2HPO_3HNa,5H_2O$ develops + 19·30 Cals., or 3·86 Cals. per molecule of water. It follows, therefore, that

the combination of a molecule of water with sodium pyrophosphite liberates more heat than the combination of a molecule of water of crystallisation with the phosphite. C. H. B.

Heat of Formation of Platinic Chloride. By L. PIGEON (*Compt. rend.*, **110**, 77—80).—In order to avoid the presence of nitrogen oxides and the difficulties of removing them, platinic chloride was prepared by passing chlorine into ammonium platinochloride suspended in water heated at 110°. The solution was evaporated by a gentle heat and finally in a vacuum, when orange-red, deliquescent prisms of hydrogen platinochloride, $H_2PtCl_6 + 6H_2O$, were obtained. If this salt is heated at 360°, it loses water and hydrogen chloride, but first melts and then intumesces. If, however, it is allowed to remain over potash at the ordinary temperature, it loses 4 mols. H_2O, and the dehydrated salt when heated in chlorine at 360° does not melt, but gives off water and hydrogen chloride and yields the tetrachloride as a brown powder. When the latter is heated only to dull redness, it decomposes, and the upper part of the crucible, &c., is studded with small, distinct crystals of platinum, a result similar to that obtained by Moissan with platinum fluoride.

Anhydrous platinum chloride dissolves in dilute hydrochloric acid with development of heat—

$$PtCl_4 \text{ solid} + 2HCl \text{ diss.} = H_2PtCl_6 \text{ diss. develops} + 24{\cdot}8 \text{ Cals.}$$

A further quantity of hydrochloric acid produces no thermal disturbance. Combining this result with Thomsen's value for the heat of formation of dissolved hydrogen platinochloride from solid platinum, gaseous chlorine, and dissolved hydrochloric acid (84·6 Cals.), the following results are obtained:—

Pt solid + Cl_4 gas = $PtCl_4$ solid	develops	+59·8 Cals.
$PtCl_4$ solid + 2KCl solid = K_2PtCl_6	,,	+29·7 ,,
$PtCl_4$ solid + 2NaCl solid = Na_2PtCl_6....	,,	+13·9 ,,

The heat of dissolution of hydrogen platinochloride, $H_2PtCl_6 + 6H_2O$, is +4·34 Cals. C. H. B.

Influence of Certain Groups on the Thermochemical Value of the Hydroxyl- and Carboxyl-groups in the Aromatic Series. By P. ALEXÉEFF and E. WERNER (*Bull. Soc. Chim.* [3], **2**, 717—728). —The introduction of the NO_2 group into a phenol augments the heat of neutralisation by alkaline hydroxides, the increase being greatest for the orthonitro- and least for the metanitro-derivative, whilst the introduction of nitrogen into a phenol, as in the case of the azophenols, determines a diminution which is greatest for the para-derivative.

The substitution of NO_2 for H in the benzoic acid molecule causes an increase in the heat of neutralisation for the ortho- and the para-derivative, whilst the heat evolved by the meta-compound is diminished, and in the azobenzoic acids the nitrogen appears to exercise a diminishing effect, which is greatest for the para-derivative.

With the amidobenzoic acids, the influence of the NH_2 group is to

diminish the heat of neutralisation in the descending order, ortho, para, meta.

The substitution of an alkyl radicle for hydrogen also diminishes the heat of neutralisation, but a subsequent introduction into the molecule of NO_2 causes an increment, and in the cases of azocumic and hydrazocumic acids the introduction of nitrogen and of the NH-group again raises the heat of neutralisation.

Numerous experimental data are given which bear out the above conclusions. T. G. N.

New Form of Mixing Calorimeter. By S. U. PICKERING (*Phil. Mag.* [5], **29**, 247).—The apparatus consists of an oblong platinum vessel, divided into two compartments of 400 c.c. capacity by means of folding doors, which are pressed against a framework by two pairs of bow-shaped iridio-platinum springs; a strip of india-rubber round the edges of the doors prevents leakage. A stirrer worked by an electromotor and a delicate thermometer are placed in each compartment, and as soon as the temperature in each is identical, two ebonite knobs are pressed together, whereby the lower springs are lowered below the doors, and the upper ones are raised above them, the doors then fly open, and allow the liquids to mix. The advantages consist in starting with the liquids at the same temperature, thus eliminating errors due to a comparison of two thermometers, and obviating the necessity of knowing the heat capacity of the two liquids. The two thermometers are used simply to double the value of the observation; the mean difference between the rise registered by them in a number of determinations was found to be only 0·0008°, representing 0·6 cal. S. U. P.

Gradual Alteration in Glass produced by Altering its Temperature a Few Degrees. By S. U. PICKERING (*Phil. Mag.* [5], **29**, 289).—Observations are quoted to show that a specific gravity bottle, the capacity of which had remained unaltered for six months while kept at 18°, experienced a sub-permanent contraction on being cooled to 8°. The contraction continued during several days, and, although it was not affected by a temporary heating even to 38°, it appeared that prolonged heating at this and lower temperatures restored the bottle to its original capacity. The maximum contraction observed amounted to 0·0001 of its total volume, a quantity which would be equivalent to $\frac{1}{15}$° in a mercurial thermometer. S. U. P.

Determination of Vapour-densities of Substances below their Boiling Points. By R. DEMUTH and V. MEYER (*Ber.*, **23**, 311—316).—The vapour-density of a substance can be determined at a temperature considerably below its boiling point by the ordinary displacement method of V. Meyer, provided that the vaporising bulb is filled with hydrogen, and that some means are adopted for ensuring the rapid distribution of the substance over the bottom of the vaporising bulb.

The determinations are most easily carried out when the substance is solid at the ordinary temperature; in such cases it is not weighed

out in any vessel, but is simply cast into a small rod and, after weighing, dropped into the apparatus, where it melts and is quickly distributed over the surface of the bulb. In the case of liquids the authors recommend the use of small vessels made of Wood's fusible metal, which melts quickly when introduced into the vaporising bulb, and thus ensures rapid distribution. These bulbs can be made so thin that there is no danger of breaking the apparatus. Mercury or small platinum spirals can be employed to break the fall when necessary, but sand, asbestos, &c., must not be used. If the liquid acts on Wood's metal, or if the temperature at which the experiment is to be carried out is below the melting point of the alloy, short, wide, cylindrical stoppered glass tubes can be used; as soon as the tube has been introduced into the apparatus, the liquid is made to flow out by tapping the stem of the vaporising bulb.

The capacity of the vaporising bulb should be about 100 c.c., and its diameter 30 mm.: it should be rather flat at the bottom, and the upright tube should not be more than 4 to 5 mm. wide. The quantity of substance taken should be such that its vapour occupies about 9—11 c.c.

Experiments with xylene (b. p. 140°) at 100°, nitrobenzene (b. p. 206°) at 176°, naphthalene (b. p. 218°) at 183°, paranitrotoluene (b. p. 238°) at 205°, and ether (b. p. 35°) at 17° showed that the results are as accurate as those obtained in the ordinary way with the apparatus filled with air. F. S. K.

Viscosity of Liquids. By J. WAGNER (*Zeit. physikal. Chem.*, **5**, 31—52).—The viscosity of dilute solutions of a number of salts was examined by the method employed by Arrhenius (Abstr., 1888, 336), and the results obtained by the latter, more especially the correctness of the exponential formula used by him to express the relative viscosities of solutions, were fully verified. The formula gives in all cases approximate expression to the observed values, but generally is not quite within the limit of experimental error.

The author also finds that the viscosity of dilute solutions is an additive function of the metallic and non-metallic radicles of the dissolved salt. This property, which depends on the existence of dissociated molecules in the solutions, is not as marked in the case of the viscosity as with some other of the properties of dilute solutions, but this is explained by the fact that those molecules which remain undissociated exercise their full influence on the viscosity, whereas the influence which they have in many other cases is only small. The dissociated ions have seemingly in some cases greater, and in other cases less viscosity than the original salt.

The viscosities of the different metals are compared one with another. Those of allied metals are found to be of the same order, but in these cases the viscosity decreases as the atomic weight increases. H. C.

Nature of Osmotic Pressure. By L. MEYER (*Zeit. physikal. Chem.*, **5**, 23—27).—The author objects to the term "osmotic pressure" as used by Van't Hoff (Abstr., 1888, 778). To regard this

pressure as caused by the substance which does not pass through the membrane is incorrect, as it is simply due to a larger passage of liquid in one direction than in the other. It also cannot be said to be due to dissolved substance or the solvent alone, since by altering the nature of the membrane the solvent and dissolved substance may be made to change places, one membrane being only permeable by the first, and another only permeable by the second.

H. C.

Exceptions to the Gaseous Laws in Solutions. By A. A. NOYES (*Zeit. physikal. Chem.*, **5**, 53—67).—The gaseous laws applied to dilute solutions by Van't Hoff are found to be subject to numerous exceptions, which it may be assumed are caused by a diminution of the free path of the moving molecules, owing to the space being partly occupied by the molecules of the solvent and of the dissolved substance, and also perhaps due to an attraction existing between the dissolved substance and the solvent. On these assumptions, the author finds that Boyle's law in solution must be altered to $p(v - d) = K$, p being the osmotic pressure, v the volume in litres of the solution containing a gram-molecule of the dissolved substance, and d and K being constants. This expression is found to be in very close agreement with the results obtained by Beckmann for the reduction of the freezing point in various solutions (Abstr., 1889, 11), this latter being proportional to the osmotic pressure, and therefore giving the value of p.

The reasoning by means of which the above formula is deduced gives $d = (1 - a_1)\dfrac{b - Bc}{1 - c}$, in which a_1 is a constant, B the volume of the gram-molecule, and b the volume of the molecules in a gram-molecule of the dissolved substance, and c the volume of the molecules in a litre of the solvent. The author shows that the values of d in various cases are in general agreement with the above expression, which theoretically should obtain for this constant.

Although in these deductions account is taken of a specific attraction between the dissolved substance and the solvent, the same result is obtained if this be neglected, so that seemingly it does not exist.

H. C.

Solubility of Saline Mixtures. By A. ÉTARD (*Bull. Soc. Chim.* [3], **2**, 729—734).—When a small quantity of water acts on excess of sodium and potassium chlorides, the curve expressing the amount of mixed salts contained by the resulting solutions is rectilinear, and from its angular coefficient, the author finds that the temperature at which water would disappear from the solution is 738°, which is the melting point of potassium chloride (Carnelley); and the respective weights of potassium chloride and of sodium chloride which would be present at this temperature are calculated to be 16·7 per cent. of sodium chloride and 83·3 of potassium chloride. These weights contain sensibly equal amounts of metalloïd and of metals, thus:—

NaCl	16·7 =	Na	6·58 +	Cl	10·1
KCl	83·3 =	K.....	43·6 +	Cl	39·6
	100·0		50·18		49·7

Moreover, these numbers are such as correspond with the association of the same number of chlorine and of potassium + sodium atoms—

$$\left(\frac{39\cdot6 + 10\cdot1}{35\cdot5}\right)\text{Cl} = 1\cdot408 \cdot \frac{43\cdot6}{39}\text{K} + \frac{5\cdot6}{23}\text{Na} = 1\cdot408.$$

The curves representing the chlorine and potassium + sodium present in the mixed salts dissolved, are also right lines which meet at 738°. These results may have some relation to the hypothesis of Arrhenius. T. G. N.

Substitution of Salts in Mixed Solutions. By A. Étard (*Compt. rend.*, **110**, 186—188).—The solubility of potassium iodide between −22° and 0° is represented by a line sharply inclined to the axis of temperature; from 0° to 108°, by another right line ($0\cdot1257t$); and from 108° to 220°, by another right line ($0\cdot0603t$). Calculation of the *limiting temperature* by extrapolation gives 637°, practically identical with the melting point of the iodide, 639°.

As a general rule with all salts, the higher the temperature the less is the inclination of the right line representing the solubility to the axis of temperature, and the irregularities in solubility are observed below 130°, a temperature above which hydrates rarely exist.

If a small quantity of water is brought into contact with a mixture of potassium iodide and bromide, the total quantity of salt dissolved is the same as if the iodide alone were present, and the limiting temperature is the melting point of the iodide. The bromide obeys the law of solubility of the iodide, and at the limit of solubility the ratio of bromide to iodide in the solution would be 33·6 : 66·4.

Potassium chloride mixed with the iodide behaves in a precisely similar manner, and at the limit of solubility the ratio of chloride to iodide would be 20 : 80.

Potassium bromide and chloride behave similarly, the ratio at the limit of solubility being KCl : KBr. : : 25 : 75.

The phenomena might be explained by supposing that mutual substitution took place, but the ratios of the constituents of the dissolved mixtures have no direct relation to their molecular weights.

C. H. B.

Molecular Constitution of Compounds at their Critical Point. By P. A. Guye (*Compt. rend.*, **110**, 141—144).—From the definitions, the value of b in the equation of Van der Waals should be proportional to the molecular refractive power of the substance, which the author calculates from the expression $R = \dfrac{N^2-1}{(N^2+2)d}$. Now, the critical coefficient χ, or the ratio of the absolute critical temperature to the critical pressure, is also proportional to the value of b, and therefore to the molecular refractive power. Hence, if f be a constant for all substances, we have—

$$(1.)\quad \frac{MR}{\chi} = f.$$

The author has calculated the molecular refractive power of all substances for which the other data required were known. The value of f varies between 1·6 and 2·0, the mean being 1·8. The variations from the mean amount to about 10 per cent., which is also the possible error in the magnitude of χ. This holds good through a wide range of critical temperatures, and for very different substances. It is important to note that if the refractive power is calculated to the molecular weight, the value of f is 1·8, but if it is calculated to the equivalent, the value of f is sometimes 1·8 and sometimes 0·9.

The relation may also be written in the form—

$$(2.)\ \mathrm{M} = f\frac{\chi}{\mathrm{R}},$$

and, hence, the molecular weight of a substance at its critical point can be calculated if the critical coefficient and the refractive power are known. The results obtained show that the molecular weights of liquids at their critical points agree with those calculated according to Avogadro's law.

It is evident that the relation (1.) can only hold good if the molecular refractive power and the critical coefficient of a substance are characterised by the same variations, and it follows that the knowledge of the critical coefficient of a substance only is sufficient for the determination of its molecular weight at the critical point. The molecular refractive power can be calculated from the coefficients of refraction of the constituent atoms, and if these coefficients are divided by 1·8, a new series of numbers is obtained, which the author terms *critical atomic coefficients*, and from these the critical coefficient of a substance can be calculated. The values obtained in this way agree with the experimental numbers, within the limits of experimental errors.

It is always possible, therefore, to calculate a value for the critical coefficient with such an approximation to accuracy that on comparison with the experimental number a choice can be made from several possible formulæ of that one which most accurately represents the molecular weight of the substance at its critical point. C. H. B.

Equilibrium in Homogeneous Solutions when unequally heated. By P. VAN BERCHEM (*Compt. rend.*, **110**, 82—84).—Hydrochloric acid and ammonia solutions respectively were enclosed in sealed tubes. the upper parts of which were heated. The contents of the hot and cold parts of the tube were analysed, and it was found that there is a decided concentration of the gases in the cold part of the solution. This result is not due to distillation, for if the hot and cold portions of the liquid are separated by air, the difference in composition becomes very much greater. C. H. B.

Residual Affinity of Inorganic Salts. By B. LACHOWICZ (*Monatsh.*, **10**, 884—905; compare Abstr., 1888, 1281, 1889, 569).—Most organic bases give precipitates of definite composition when shaken with solutions of salts of the heavy metals; in the table given

below, the sign + denotes that such a precipitate is formed between the corresponding base and salt.

	Piperidine.	Pyridine.	Quinoline.	Aniline.	Orthotoluidine.	Paratoluidine.	β-Naphthylamine.	α-Naphthylamine.	Phenylhydrazine.	Methylaniline.	Dimethylaniline.	Xylidine.
$AgNO_3$	+	+	+	+	+	+	+					
$CuCl_2$.....	+	+					+	+				
HgCl......		+	+		+		+			trace	+	
$CuSO_4$.....			+		+	+						
$ZnSO_4$									+			
$MgSO_4$									+			
$Cu(NO_3)_2$.						+						
$PbNO_3$			+		+	+					+	+
$NiCl_2$.....			+									
$CdCl_2$					+	+						

It appears that all the salts of the heavy metals with strong acids form compounds with organic bases, and that these are analogous to compounds formed from the combination of acids with bases. The various salts of the same acid have different affinities for organic bases, and the affinity varies inversely as the basicity of the metal, and inversely as the heat of formation of the salts formed from the acid and the metals. G. T. M.

Inorganic Chemistry.

Preparation of Chlorine Gas for Laboratory Purposes. By P. Klason (*Ber.*, **23**, 330—337).—I. From manganese peroxide and hydrochloric acid.—According to the author's experiments, the different varieties of pyrolusite yield from 75—85 per cent. of the theoretical quantity of chlorine. For each kilo. of peroxide, about 4 litres of 36 per cent. hydrochloric acid are necessary, the greatest possible yield of chlorine being 174 grams per litre; as a general rule, however, only 125—140 grams are obtained. For the preparation of the gas in considerable quantities, the author recommends the use of an earthenware apparatus, the principle of which is similar to Kipp's. The central chamber is filled with 3 kilos. of pyrolusite in small pieces, 2 litres of concentrated hydrochloric acid added, and the whole heated on the water-bath. (In order to allow space between the apparatus and the bottom of the water-bath, the former is constructed with small feet.) The stream of chlorine can

be regulated exactly, and when the gas ceases to come off, the spent acid is removed, and 2 litres of fresh acid introduced. The quantity of pyrolusite originally taken is sufficient to use up 12 litres of acid. In order to prevent chlorine entering the room when the current of the gas is stopped, the upper chamber is connected with a funnel containing soda crystals.

II. From sodium chloride, pyrolusite, and sulphuric acid.—It is usually supposed that in this reaction the whole of the chlorine is evolved in the free state; detailed experiments have, however, shown that this is not the case, but that the reaction which takes place is as follows:—

$$4NaCl + MnO_2 + 3H_2SO_4 = 2NaHSO_4 + Na_2SO_4 + MnCl_2 + 2H_2O + Cl_2.$$

The necessary proportions are, therefore, 5 parts of pyrolusite, 11 parts salt, and 14 parts of sulphuric acid diluted with an equal volume of water.

III. From pyrolusite, hydrochloric and sulphuric acids.—The instructions usually given for the preparation of chlorine by this method are to take 1 part of pyrolusite, 2 of hydrochloric acid of sp. gr. 1·14, and 1 part of sulphuric acid mixed with an equal bulk of water, the reaction being supposed to take place according to the equation—

$$MnO_2 + 2HCl + H_2SO_4 = MnSO_4 + 2H_2O + Cl_2.$$

As in the foregoing case, this equation is quite incorrect, only 65 per cent. of the chlorine being obtained in the free state.

IV. From bleaching powder and hydrochloric acid.—In this method it is unnecessary to mix the bleaching powder with gypsum (Winkler, Abstr., 1887, 442), or to compress it into cakes (Thiele, this vol., p. 6), it being quite sufficient to put it into the central bulb of a Kipp's apparatus, and bore a hole through the cake with a glass rod.

When a small quantity only of chlorine is required, and absolute purity of the gas is not necessary, this method may be with advantage employed, but in the preparation of large quantities, it is much more advantageous to obtain it by the action of hydrochloric acid on pyrolusite, in the earthenware apparatus described above.

H. G. C.

Iodine in Solution. By H. Gautier and G. Charpy (*Compt. rend.*, **110**, 189—191).—Iodine solutions are generally classed as violet or brown, but every intermediate tint can be obtained by using different solvents. The following results were obtained with 15 different solvents: *violet*, carbon bisulphide, carbon tetrachloride, chloroform; *red*, benzene, ethylene dichloride, ethylene dibromide; *red-brown*, toluene, ethyl bromide, paraxylene, ethyl iodide; *brown*, acetophenone, acetic acid, ether, alcohol, acetone. Changes in colour are accompanied by changes in the position of the absorption bands. The spectrum of the violet solutions closely resembles that of the vapour, but is displaced towards the blue.

Cryometric determinations of the molecular weight combined with

Loeb's results with benzene and carbon bisulphide gave the following results:—

Solvent.	Mol. wt.	
Ether	507	$I_4 = 508$
Acetophenone	484	$I_3 = 381$
Benzene	341	$I_2 = 254$
Carbon bisulphide	303	

Hence, it would seem that in the brown solutions, the molecule of iodine contains 4 atoms, but this gradually splits up until it acquires in the violet solutions a value approaching that of the iodine in the state of gas (compare next Abstr.). A rise of temperature tends to make all the solutions violet. C. H. B.

Molecular Weights of Dissolved Iodine, Phosphorus, and Sulphur. By E. Beckmann (*Zeit. physikal. Chem.*, **5**, 76—82).—The molecular weights of iodine, phosphorus, and sulphur were determined from the boiling points of their solutions by the method already described (this vol., p. 323). Iodine, both in ether and in carbon bisulphide, gave numbers corresponding with the molecule I_2, a result at variance with that formerly obtained by Loeb (Trans., 1888, 805). Phosphorus dissolved in carbon bisulphide gives a molecular weight corresponding with the molecule P_4, whilst sulphur in the same solvent has a high molecular weight, corresponding approximately with the formula S_8. H. C.

Formation of Ozone and Nitrogen Acids in Combustion. By L. Ilosvay de N. Ilosva (*Bull. Soc. Chim.* [3], **2**, 734—741).—Ozone is absent from oxygen obtained by the action on potassium permanganate of concentrated sulphuric acid, the indications afforded by the usual reagents being due either to traces of chlorine contained in the permanganate, or to permanganic anhydride which is carried over.

During the active combustion of coal-gas, nitrites are always formed, and vary in amount directly as the temperature of the flame. When pure air, either alone or mixed with oxygen, is burnt in coal-gas, much nitrous and nitric acids, together with ammonia, are formed, and when air mixed with nitric oxide is similarly burnt, cyanogen is also formed. These results appear to prove that at high temperatures nitrogen has some affinity for hydrogen, oxygen, and carbon.

The author passed air over different varieties of platinum at varying temperatures, and his results prove that under no circumstances is ozone formed, and that the nitrites produced do not originate from a surface condensation, but from a catalysis, which depends on the molecular structure of the platinum and on the temperature.

When air is passed over reduced iron at 190—250°, nitrous acid is formed, but is absorbed by the yellowish-brown iron oxide, since no nitrite can be detected in the air which passes over, whereas the washings of the iron oxide yield evidence of nitrites. Although

reduced iron at 400° is not oxidised by dry air with incandescence, traces of moisture determine this result at once. T. G. N.

Combination of Hydrogen Phosphide with Boron Fluoride and Silicon Fluoride. By BESSON (*Compt. rend.*, **110**, 80—82).—Hydrogen phosphide and boron fluoride do not unite at the ordinary temperature, but combination begins at −30°, and at −50° a white solid is obtained, which becomes yellow as the temperature rises, with evolution of 2 vols. of boron fluoride and 1 vol. of hydrogen phosphide, the latter being mixed with some free hydrogen, whilst some solid hydrogen phosphide is formed. The white solid has the composition $PH_3,2BF_3$, and is decomposed by water with evolution of hydrogen and hydrogen phosphide.

Hydrogen phosphide and silicon fluoride combine only under pressure, and at −22° under a pressure of 50 atmos. a white, crystalline solid is obtained. The best yield is obtained with the proportion of gases given, but the solid is also formed when the gases are mixed in equal volumes or two volumes of silicon fluoride and one of hydrogen phosphide, but with one volume of the former and two of the latter, or three of the former and one of the latter, no solid is obtained even at −40°. The solid compound has the composition $2PH_3,3SiF_4$. C. H. B.

Different Forms of Graphitic Carbon and their Derivatives. By BERTHELOT and P. PETIT (*Compt. rend.*, **110**, 101—106, 106—109). —Graphite formed in various ways was converted into the corresponding graphitic oxide by the method described some time ago (*Ann. Chim. Phys.* [4], **19**, 409). In the various analyses given, the ash has been deducted.

Graphite from Cast Iron.—The *graphitic oxide* has the composition C, 62·7; H, 1·3; O, 36·0; which agrees with the empirical formula $C_7H_2O_3$, and for purposes of comparison may be represented by the rational formula $C_{28}H_8O_{12}$. Saturation with baryta-water indicates mono-basicity for the empirical formula, and tetra-basicity for the rational formula. It deflagrates suddenly if heated to a certain temperature, but if carefully heated in a sealed tube, it yields pyrographitic oxide, water, carbonic oxide, and carbonic anhydride, the ratio between the two latter being 2 vols. to 3 vols.

The *pyrographitic oxide* is black, and has the composition C, 86·55; H, 0·70; O, 12·75, and may be represented by the formula $C_{46}H_6O_5$.

Amorphous Graphite or Plumbago.—The *graphitic oxide* has the composition C, 56·2; H, 1·5; O, 42·1; N, 0·1; which agrees with the formula $C_{56}H_{22}O_{31}$, or $C_{22}H_8O_{12}$. When heated in a sealed tube, it yields water, carbonic anhydride, and carbonic oxide, in the ratio of three vols. to two, and a *pyrographitic oxide*, which contains C, 83·85; H, 0·72; O, 15·43 per cent., and therefore has the formula $C_{44}H_6O_6$.

Electric Graphite.—Carbon converted into graphite in the electric arc yields a *graphitic oxide* of the composition C, 51·95; H, 1·55; O, 46·35; N, 0·15, which agrees with the formula $C_{28}H_{10}O_{19}$, or $C_{16}H_6O_{11}$.

The difference between the three graphitic oxides becomes evident

if the hydrogen is assumed to be present in the form of water, and the amount of carbon is supposed to be the same in all cases.

From cast iron	$C_{56}O_{16} + 4H_2O$
From plumbago	$C_{56}O_{20} + 5H_2O$ or $C_{44}O_{16} + 4H_2O$
From electric graphite .	$C_{56}O_{28} + 5H_2O$ or $C_{32}O_{16} + 3H_2O$

The different degrees of polymerisation of the carbon become recognisable if the results are calculated to the same amount of oxygen, the carbon-atoms being in the ratio of 56 : 44 : 32.

The graphitic and pyrographitic oxides were burnt in the calorimetric bomb in oxygen compressed to 25 atmospheres.

Graphitic Oxide from Cast Iron.—Molecular heat of combustion at constant volume, 2530·0 Cals.; at constant pressure, 2527·7 Cals., heat of formation from its elements, carbon as diamond, 388·7 Cals., carbon as graphite, 412·7 Cals. The *pyrographitic oxide:* heat of combustion at constant volume, 4479·4 Cals.; at constant pressure, 4478·8 grams; heat of formation, carbon as diamond, 66·0 Cals., carbon as graphite, 89·0 Cals.

These numbers give no exact idea of the phenomena of combustion or formation, since at the moment of formation part of the hydrogen is fixed in the form of water, with a loss of energy which cannot be estimated, but if the maximum possible value of this loss be deducted, it will be seen that the heat developed per atom of oxygen which enters into combination is only +15·3 Cals., a value much lower than the heat developed by its conversion into carbonic oxide, or still more carbonic anhydride, a fact which explains the ready decomposition of the graphitic oxide with liberation of carbonic oxide and anhydride, and the retention of part of the energy by the pyrographitic oxide, which is thus an endothermic compound, about −3·0 Cals. being absorbed per atom of carbon. The conversion of the graphitic oxide into pyrographitic oxide liberates +162·6 Cals., and if the mean specific heat of the product is taken as 0·25, the temperature of decomposition will be about 600°.

Graphitic Oxide from Plumbago.—Molecular heat of combustion at constant volume, 2637·7 Cals.; at constant pressure, 2633·8 Cals. Heat of formation from diamond, +351·6 Cals., from graphite, +365·6 Cals. The *pyrographitic oxide:* Heat of combustion at constant volume, 4157·0 Cals.; at constant pressure, 4156·1 Cals. Heat of formation from diamond +200·1 Cals., from graphite, +222·1 Cals.

Graphitic Oxide from Electric Graphite.—Molecular heat of combustion at constant volume, 2606·05 Cals.; at constant pressure, 2602·0 Cals. Heat of formation from diamond, +383 Cals., from graphite, +397 Cals.

The heats of formation of the graphitic oxides are very different, and characterise the different species. If these heats of formation are calculated to the same weight of carbon, they are represented by the numbers 13·9, 12·5, and 13·7 respectively. These values are almost equal, although the corresponding amounts of oxygen are in the ratio of 4 : 5 : 7, and this agreement in the quantity of heat developed by very different degrees of oxidation shows clearly the

important differences between the various graphitic radicles and the oxides to which they give rise. C. H. B.

Combination of Alkali Metals with Ammonia. By H. W. B. ROOZEBOOM (*Compt. rend.*, **110**, 134—137).—A theoretical discussion of the observations of Joannis (this vol., p. 209) on the dissociation of sodammonium or potassammonium, which the author regards as analogous to the dissociation of a mixture of tetrahydrated calcium chloride, $CaCl_2 + 4H_2O$, and its saturated solution (*Rec. Trav. Chim.*, 8, 1—146). C. H. B.

New Hydrate of Potassium Hydrogen Sulphate. By J. B. SENDERENS (*Bull. Soc. Chim.* [3], **2**, 728).—When an aqueous solution of potassium hydrogen sulphate is evaporated at a gentle heat to such an extent that on removal of the flame a solid mass is obtained, there will appear on the surface of the mass after some time a layer of arborescent crystals, which have the composition $HKSO_4 + 5\frac{1}{2}H_2O$; these melt at 30°, and deliquesce so soon as the arborescence is completely developed. The formation is dependent on the degree of concentration of the mother liquor, and on the temperature of the laboratory. T. G. N.

Solubility of Calcium Carbonate in Fresh and Sea Water. By W. S. ANDERSON (*Proc. Roy. Soc. Edin.*, **16**, 319—324).—Iceland spar is less soluble in sea water than the other forms of carbonate, and it is less soluble in sea than in fresh water, the former dissolving 0·0082 gram per litre, whilst the latter, free from carbonic anhydride, takes up 0·251 gram; but the form in which the calcite is presented, whether massive or in powder, has no notable effect on its solubility in sea water, whereas in distilled water the powdered spar is soluble to double the amount. When sea water remains over calcite for some time, a portion of the dissolved carbonate is precipitated. Although this may not occur generally, yet it helps to account for the gradual petrifaction of the porous masses of dead coral reef in comparatively shallow waters. Carbonated water dissolves calcite readily; the more finely divided it is, the greater the solubility. Of the massive form, 0·0815 gram per litre is dissolved in 24 hours, and of the powdered, 0·472 gram. A series of experiments were undertaken with a view to throw light on the condition in which the carbonate is present in sea water, and for this purpose a hard variety of coral skeleton (*Oculina coronalis*) was finely powdered, and the solution allowed to act on portions of it separately for four days. The solubility was found to be greater in distilled than in sea water, the magnesium salts, chloride and sulphate, dissolving the largest quantity, and calcium sulphate the least; in fact this salt seems to retard solubility. Solution of magnesium chloride dissolves, and then throws out the carbonate in crystalline form, and this action shows that there is no interaction between magnesium chloride and calcium carbonate, as if there were, magnesium carbonate would be precipitated; sea water acts in a manner similar to magnesium chloride. 0·6 gram per litre being dissolved, and a portion being afterwards precipitated. This is not due

to carbonic anhydride, for artificial sea water free from gas acts in the same way. Solutions of the individual salts dissolved more of the coral skeleton than did the normal or artificial sea water; this appears due to the action of calcium sulphate, as before stated. The author considers, therefore, that calcium carbonate is present in sea water as such, and is there simply owing to its solubility in the river water flowing into the sea, the salts present helping or retarding the solution, as the case may be. E. W. P.

Prolonged Action of Sea Water on Pure Natural Magnesium Silicates. By A. JOHNSTONE (*Proc. Roy. Soc. Edin.*, 16, 172—175). —Sea water dissolves pure steatite in small quantities, with separation of silica, and this solution is attributed to the sodium chloride in the water: $Mg_4Si_5O_{14} + 8H_2O + 8NaCl = 4Na_2SiO_3,8H_2O + 4MgCl_2 + SiO_2$. Pure white talc is also slightly soluble, but the common green variety, which contains iron, is more easily dissolved.

E. W. P.

Reduction of Oxygen Compounds by Magnesium. By C. WINKLER (*Ber.*, 23, 120—130).—In this paper the author gives an account of the action of magnesium on the oxides of the metals of Mendeléeff's second group; the experiments were carried out in the manner previously described (this vol., p. 331), but in some cases the behaviour of the hydroxide, as well as that of the oxide, was studied.

Beryllium oxide (2 mols.) is reduced, but only partially, by magnesium (1 mol.), and the reaction is not very energetic, although the mixture glows feebly, and some of the magnesium is volatilised. The grey mass obtained is not acted on by boiling water, but when warmed with soda, hydrogen is slowly evolved. It dissolves in hydrochloric acid and in nitric acid, hydrogen being rapidly evolved, and when heated in the air it glows brightly. When treated with chlorine at a high temperature, beryllium chloride sublimes.

In heating metallic oxides with powdered magnesium, the latter is, to a slight extent, converted into the nitride by the nitrogen of the air; the formation of nitride is proved by the evolution of ammonia, when the mixture is subsequently exposed to moist air. When magnesium wire is burnt in the air, the formation of nitride does not take place, but when powdered magnesium is heated with magnesium oxide, the product gives off ammonia on warming with potash. It seems, therefore, that the presence of substances otherwise inactive, but which absorb heat, favours the formation of magnesium nitride.

Pure magnesium oxide undergoes no change when heated with magnesium, and the formation of a lower oxide was not observed.

Calcium oxide is almost completely reduced by magnesium at a red heat; the mixture turns grey, but otherwise no apparent change takes place. The residue takes fire readily when heated, burning with a brilliant, reddish flame, and it decomposes water very energetically.

When a mixture of calcium hydroxide (1 mol.) and magnesium (1 mol.) is heated in a test-tube, a brilliant, yellowish-red flame issues from the mouth of the tube, but reduction is incomplete; the residue decomposes water rapidly. When steam (most conveniently obtained

by heating crystalline calcium chloride or some other salt containing water) is passed over powdered magnesium, heated to redness in a combustion-tube, the metal glows brightly, and is quickly converted into oxide with development of heat.

Strontium oxide is slowly, and as it seems completely, reduced by magnesium; the dark coloured residue takes fire in the air, and burns with an intense, red light, and it decomposes water very energetically. Strontium hydroxide is partially reduced by magnesium below a red heat, with a slight explosion.

Barium oxide is completely, or almost completely, reduced by magnesium, a very violent reaction taking place, accompanied by vivid glowing; the residue decomposes water very energetically. Barium hydroxide resembles strontium hydroxide in its behaviour with magnesium.

Zinc oxide is reduced by magnesium at a dull red heat, with explosive violence. Cadmium oxide shows a like behaviour, and reduction is complete, but the reaction is not so violent. In the case of mercuric oxide, a violent explosion takes place, and the metal produced is completely volatilised. F. S. K.

Zinc-ammonium Compounds. By H. Thoms (*Chem. Centr.*, 1889 [2], 965; from *Pharm. Centrahalle*, **30**, 629—631).—The author criticises the formula of the zinc-ammonium carbonate obtained by G. Kassner (Abstr., 1889, 1049) in relation to the constitution of the zinc-ammonium chloride described by him (Abstr., 1887, 551), in which he holds that the nitrogen is directly combined with the zinc. If Kassner's zinc oxide ammonium carbonate is similarly constituted to the author's zinc-ammonium chloride, then it must have the formula $Zn{:}O_2{:}C(OH){\cdot}O{\cdot}Zn{\cdot}NH_3O{\cdot}C(OH){:}O_2{:}Zn$. If, however, the hydroxyl-groups are combined with the zinc, as according to Kassner they are, then the compound must have the formula

$$OH{\cdot}Zn{\cdot}O{\cdot}CO{\cdot}O{\cdot}Zn{\cdot}NH_3O{\cdot}CO{\cdot}O{\cdot}Zn{\cdot}OH,$$

and the author remarks that it is not quite clear why the excess of ammonia present in the reaction does not become combined with the zinc hydroxyl-group. J. W. L.

Cerium Hydrogen Sulphate. By G. Wyrouboff (*Bull. Soc. Chim.* [3], **2**, 745—747).—The hydrated and anhydrous varieties of the lower cerium oxide dissolve in concentrated sulphuric acid, and the solution, on evaporation, deposits small, brilliant, transparent needles. When the evaporation is continued until no more sulphuric anhydride is evolved, care being taken that the temperature of decomposition of the salt is not reached, a perfectly pure crystalline substance is obtained, which contains in 100 parts CeO 38·69, and SO_3 55·58.

Taking the atomic weight of cerium as 94·4, this corresponds with the formula $CeSO_4,H_2SO_4$, and insomuch as it is quite stable in dry air, but very hygroscopic, it corresponds with the acid sulphates of the magnesium series, and consequently lends additional support to the view that cerium forms a monoxide, and has the at. wt. 94·4, as

determined by Bührig, and not the at. wt. 141·4, suggested by Mendeléeff, which corresponds with its forming a sesquioxide, Ce_2O_3, since there is no sesquioxide known from which an acid sulphate is derived. T. G. N.

Preparation of Very Active Platinum-black. By O. Loew (*Ber.*, **23**, 289—290).—Very active platinum-black can be conveniently prepared as follows:—An aqueous solution (50 to 60 c.c.) of platinic chloride (50 grams) is mixed with 40 to 45 per cent. of formaldehyde solution (70 c.c.), the mixture cooled well, and then sodium hydroxide (50 grams) dissolved in water (50 grams) gradually added; after keeping for 12 hours the solution is filtered. A yellow liquid, from which a small quantity of platinum is deposited on boiling, first passes through the filter, but as soon as most of the salts have been washed out of the residue, the filtrate assumes a deep black colour. The process is interrupted at this stage for several hours because the residue soon absorbs oxygen, the temperature rising to 36—40°, and the washings then pass through colourless. As soon as oxidation is complete, the residue is washed until completely free from sodium chloride, pressed, and dried over sulphuric acid.

If the deep-black filtrate referred to above is submitted to dialysis in absence of air, a black, transparent liquid is obtained which is stable in absence of air; on exposure to the air, however, this liquid gradually becomes colourless, and a small quantity of a black powder is deposited. The black solution decomposes hydrogen peroxide very energetically, and when mixed with alcohol or shaken with air, the odour of aldehyde is immediately perceptible. These and other experiments seem to show that this black liquid is a solution of atomic platinum containing small quantities of organic platinum compounds. F. S. K.

Mineralogical Chemistry.

Pseudomorphs of Native Copper after Azurite. By W. S. Yeates (*Amer. J. Sci.*, **38**, 405—407).—The author describes some specimens of copper from Grant Co., New Mexico. The substance was very brittle, and had a sp. gr. of only 4·15. The surface of the crystals was coated with kaolin, and this mineral was also intimately mixed with the copper particles. The tabular crystals had the form of those of azurite from Arizona. This was confirmed by measurements of the angles. The copper is thus a pseudomorph after azurite. The latter must have lost its carbonic anhydride and water in the presence of some reducing agent, probably volcanic gases, leaving the copper in a spongy state, and upon it the kaolin was deposited, and forced by pressure into the pores of the spongy mass.

B. H. B.

Arsenical Pyrites. By F. v. SANDBERGER (*Jahrb. f. Min.*, 1890, i, Mem. 99—101).—The occurrence of arsenical pyrites in small crystals having the form ∞P, $\frac{1}{4}\breve{P}\infty$, at Goldkronach, has long been known. Analysis of this mineral yielded—

S.	As.	Sb.	Fe.	Ag.	Total.	Sp. gr.
20·84	41·36	3·73	34·07	0·002	100·002	6·09

The mineral is of interest on account of its unusually high percentage of antimony.

A second interesting variety of arsenical pyrites occurs at Neusorg, in the Fichtelgebirge. On analysis, it gave the following results:—

S.	As.	Fe.	Ni.	Co.	Total.	Sp. gr.
17·27	42·89	34·64	4·38	trace	99·18*	5·96

In 1848 Breithaupt directed attention to the fact that certain arsenical pyrites contain nickel, but none of the varieties he mentioned contains more than 1 per cent. of that metal. B. H. B.

Artificial Formation of Malachite. By A. DE SCHULTEN (*Compt. rend.*, **110**, 202—204).—A solution of precipitated copper carbonate in ammonium carbonate is heated on a water-bath for eight days in flasks filled up to the neck, the water being renewed as it evaporates. As the ammonium carbonate volatilises, a green, crystalline crust separates on the sides of the flask, and soon becomes covered with crystals of malachite, $CuCO_3,Cu(OH)_2$, containing CuO, 71·33; CO_2, 19·72; H_2O, 8·95 = 100; sp. gr. at 15° = 3·86, that of the mineral varying from 3·7 to 4·1. Artificial malachite easily scratches calcite, but is scratched by fluorspar, and its hardness is 3·5—4·0. Its crystalline form is identical with that of the natural mineral. C. H. B.

New Variety of Aluminite. By K. FLUG (*Jahrb. f. Min.*, 1890. i. Ref. 18, from *Verh. Russ. Min. Ges.*, **23**, 116—125).—The mineral examined, to which the author assigns the name of *ignatieffite*, was found in the Bachmuth district, in the government of Ekatrinoslav. On analysis it yielded—

SiO_2.	Al_2O_3.	SO_3.	P_2O_5.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	C.	H_2O.
3·33	36·39	30·57	3·83	0·32	1·40	0·23	6·37	2·89	1·50	12·72

B. H. B.

Native Iron Sulphates from Chili. By J. B. MACKINTOSH (*Amer. J. Sci.*, **38**, 242—245).—The author gives the results of analyses of a series of native iron sulphates, several of which have not yet been described. Four of the sulphates are well-known species. The first analysis refers to coquimbite, 1*a* being amethystine, crystalline, and transparent; 1*b*, amethystine, massive, and translucent; and 1*c*, white, massive, and opaque. The analyses of these three varieties all lead to the same formula, $Fe_2O_3,3SO_3,9H_2O$. The other well-known species are: (2) copiapite, sp. gr. 2·118, formula,

$$91\{2Fe_2O_3,5SO_3,18H_2O\} + 22\{FeSO_4 + H_2O\} + 5(Na_2SO_4 + H_2O);$$

* 99·27 in original.

(3) roemerite, brown, crystalline, sp. gr., 2·15, formula,

$$FeO,Fe_2O_3,4SO_3,13·7H_2O\ ;$$

(4) amarantite, red, crystalline, sp. gr. 2·005, formula,

$$Fe_2O_3,2SO_3,7H_2O.$$

Of the new minerals, the first (analysis 5) occurs associated with copiapite and amarantite, in pulverulent, orange flakes. Its formula is $Fe_2O_3,2SO_3.4H_2O$. *Ferronatrite* (analysis 6) occurs in stellate groups of a pale, whitish-green colour, associated with copiapite and coquimbite. This new mineral is analogous to kroehnkite (Abstr., 1889, 680), the relationship being shown by the formulæ—

Kroehnkite	$3(Na_2O,CuO,2SO_3,2H_2O)$
Ferronatrite	$3Na_2O,Fe_2O_3,6SO_3,6H_2O$.

Associated with these minerals are several white pulverulent sulphates, which are apparently alteration-products. The formulæ of the three powders analysed are—

(7) $4FeO,Fe_2O_3.6SO_3.19H_2O$.
(8) $428(FeSO_4,H_2O) + 71Na_2SO_4 + 40(2Fe_2O_3,5SO_3.4H_2O)$.
(9) $487(FeSO_4,H_2O) + 5Na_2SO_4 + 16(2Fe_2O_3,5SO_3,18H_2O)$.

	SO_3.	Fe_2O_3.	Al_2O_3.	FeO.	Na_2O.	K_2O.	Insol.	H_2O.
1*a*	43·40	22·17	4·39	—	0·25	—	—	29·79
1*b*	42·90	26·10	1·65	—	0·27	—	—	29·08
1*c*	42·32	28·10	0·91	—	—	—	—	28·67
2	39·03	29·16	—	1·56	0·31	—	—	29·94
3	40·19	19·40	—	9·52	0·14	—	—	30·85
4	36·15	35·69	0·21	—	0·51	—	—	27·44
5	41·24	41·22	—	—	—	—	—	17·54
6	50·25	17·23	0·43	—	18·34	0·40	2·00	11·14
7	38·00	12·16	—	22·51	0·58	—	—	26·75
8	47·90	5·64	0·65	30·81	4·42	—	—	10·58
9	45·61	5·14	—	35·05	0·33	—	—	13·87

(For recent analyses of South American iron sulphates, see Abstr., 1888, 923). B. H. B.

Minerals from Atacama. By L. DARAPSKY (*Jahrb. f. Min.*, 1890, i, Mem. 49—70).—1. *Aromite.*—In the "pampa de Aroma," in the northern portion of Tarapacá, an alum occurs which on analysis gave the following results :—

Al_2O_3.	MgO.	SO_3.	H_2O.
5·00	12·71	33·71	48·58

These results lead to the formula $Al_2O_3,6MgO,9SO_3,54H_2O$. This new variety forms with the known magnesia alums a series in which the percentage of water gradually increases :—

Pickeringite........	$(MgSO_4),(Al_2O_3,3SO_3),24H_2O$
Sesquimagnesia alum.	$1\frac{1}{2}(MgSO_4),(Al_2O_3,3SO_3),26\frac{1}{2}H_2O$
Picroalaunogen......	$2(MgSO_4),(Al_2O_3,3SO_3),28H_2O$
Sonomaite..........	$3(MgSO_4),(Al_2O_3,3SO_3),33H_2O$
Aromite............	$6(MgSO_4),(Al_2O_3,3SO_3),54H_2O$.

2. *Iron Sulphates.*—The author gives the results of the analyses of seven varieties of iron sulphate. The analytical results are given in the following table:—

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*
Fe_2O_3.....	30·00	35·62	36·86	28·18	32·13	18·22	18·13
Al_2O_3.....	—	—	—	2·95	—	3·01	—
FeO......	—	—	—	—	—	—	8·30
Cu_2O.....	8·27	—	—	—	—	—	—
SO_3.......	33·05	36·20	36·85	38·47	30·60	41·15	36·19
H_2O......	26·81	28·33	26·34	29·50	35·74	27·64	34·30
CaO......	—	—	—	trace	—	4·10	0·45
MgO.....	—	—	—	0·15	—	5·62	—
Insoluble..	1·83	—	0·53	0 78	1·41	—	2·63
Total.....	99·96	100·15	100·58	100·03	99·88	99·74*	100·00

a. Paposite, a mineral first described by Stüven, who assigned to it the formula $Fe_2O_3,2SO_3,4H_2O$. The author's formula is

$$2Fe_2O_3,3SO_3,10H_2O.$$

b. Amarantite, first described by Frenzel. Formula,

$$Fe_2O_3,2SO_3 + 7H_2O.$$

c. Hohmannite, a mineral also described by Frenzel, is intimately mixed with a laminated mass, which gave on analysis the results stated in the table. *d.* Copiapite, formula, $Fe_2O_3.2\frac{1}{2}SO_3,8H_2O$. *e.* Fibroferrite, formula, $Fe_2O_3,2SO_3,10H_2O$. *f.* Rubrite, formula, $Fe_2O_3,2SO_3,3H_2O$. *g.* Botryogen, formula,

$$2(Fe_2O_3,3SO_3),(FeO,SO_3),32H_2O.$$

[Compare Chilian iron sulphates, preceding abstract].

3. *Thenardite.*—This mineral gave on analysis:—

SO_3.	H_2O.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	Cl.	Insol.	Total.
54·24	0·73	0·06	0·20	0·22	0·07	41·66	0·36	2·46	100·00

B. H. B.

Uraninite. By W. F. HILLEBRAND (*Amer. J. Sci.*, **38**, 329).—The author has noticed that on treatment of uraninite with an acid, nitrogen is given off in quantity amounting to 1 to 2 per cent. of the weight of the mineral. No clue has yet been discovered as to the reaction by which the gas is given off. B. H. B.

Barysite, a New Lead Silicate. By A. SJÖGREN and C. H. LUNDSTRÖM (*Jahrb. f. Min.*, 1890, i, Ref. 24—25; from *kong. Vetenskaps-Akad. Förhandl.*, 1888, 7).—In the iron ore vein of the Harstig

* 99·81 in original.

mine, a lead silicate occurs, which on account of its high specific gravity has been named *barysite*. It is associated with yellow garnet, calcite, tephroite, hedyphane, and lead carbonate. Its sp. gr. is 6·55. The mean of several analyses is—

SiO_2.	PbO.	MnO.	FeO.	CaO.	MgO.
17·07	78·26	3·51	0·16	0·41	0·59

Formula, $3RO,2SiO_2$, in which RO is PbO with a small proportion of MnO, MgO, and CaO. The mineral occurs in hexagonal, silver-white crystals, with a basal cleavage, and a hardness of 3.

B. H. B.

Gadolinite, Cacoclasite, and Monazite. By F. A. GENTH (*Amer. J. Sci.*, **38**, 198—203).—An examination of a shining, black mineral from Burnett Co., Texas, proved it to be *gadolinite*, a mineral which, excepting that from Colorado described by L. G. Eakins, has never been observed in the United States. Analysis gave the following results (I):—

	SiO_2.	Al_2O_3.	Ce_2O_3.	$(DiLa)_2O_3$.	$(YEr)_2O_3$.	MnO.	FeO.	BeO.	MgO.
I.	22·87	0·28	2·65	5·22	44·35	0·22	13·69	9·24	0·07
II.	22·80	0·31	2·66	5·01	44·45	0·18	12·93	9·19	0·11

	CaO.	Na_2O.	K_2O.	Ignition.	Insoluble.	Total.
I.	0·64	0·20	0·15	0·72	—	100·30
II.	0·71	0·23	0·12	0·79	0·93	100·42

II shows the results of an analysis of a similar mineral received by the author from Llano Co., Texas.

In 1883 H. Carvill Lewis described, under the provisional name of *cacoclasite*, peculiar white crystals embedded in blue calcite at Wakefield, Quebec, Canada. The author has submitted this substance to further examination, and his analyses tend to show that cacoclasite cannot be regarded as a distinct species, but that it is a mixture of quartz, calcite, apatite, and unknown minerals in various proportions. It has the form of scapolite, and has resulted from the alteration of that mineral.

At the Villeneuve Mica Mine, Quebec, Canada, an interesting variety of monazite has recently been met with. It has a sp. gr. of 5·233, a reddish-brown colour, and an indistinct cleavage. Analysis gave the following results:—

H_2O.	SiO_2.	ThO_2.	P_2O_5.	Fe_2O_3.	Ce_2O_3.	$(LaDi)_2O_3$.	$(YEr)_2O_3$.
0·78	0·91	12·60	26·86	1·07	24·80	26·41	4·76

MgO.	CaO.	Total.
0·04	1·54	99·77

B. H. B.

Yttria and Thoria Minerals from Llano Co., Texas. By W. E. HIDDEN and J. B. MACKINTOSH (*Amer. J. Sci.*, **38**, 474—486).—In 1886 the first piece of gadolinite was found on the west bank of the Colorado river, Llano Co., Texas. Subsequently masses of this rare mineral were obtained, in the aggregate, not less than 500 kilos. The

various ores of the rare earths are found in a coarse-textured, deep-red granite, traversed by quartz veins. The list of mineral species identified includes quartz, hyalite, orthoclase, albite, biotite, muscovite, magnetite, martite, gadolinite (several varieties due to alteration), fergusonite (three varieties of hydrous species), allanite, molybdenite, molybdite, cyrtolite, fluorspar, gummite, a carbonate of the rare earths (tengerite?), a thorium yttrium lead uranate, a hydrous uranium thoro-silicate, and a yttrium thorium silicate. The last-named mineral is termed by the authors *yttrialite*. It has a sp. gr. of 4·575 and a hardness of 5 to 5·5. When heated, it decrepitates and falls to powder. These characteristics serve to distinguish it from gadolinite, from which it differs in containing twice as much silica and no glucina. Analysis yielded—

SiO_2.	PbO.	ThO_2.	MnO.	FeO.	CaO.	Al_2O_3.	Ce_2O_3.
29·17	0·85	12·00	0·77	2·89	0·60	0·55	1·86

Yttria earths.	$(LaDi)_2O_3$.	UO_3.	Ignition.	Total.
46·50	2·94	0·83	0·79	99·75

By successive precipitations with sodium sulphate, several fractions of the yttria earths were obtained; the atomic weight of each fraction was determined, showing successive increase after each separation. The fractionation was discontinued after the fourth separation, but the atomic weight shows that the lanthanum and didymium are still mixed with an earth of higher atomic weight. The results were as follows:—

	Percentage.	Atomic weight.
(A.) Y_2O_3	22·67	110·3
(B.) Y_2O_3	5·30	110·5
(C.) Y_2O_3	4·50	114·9
(D.) Y_2O_3	14·03	120·0
$(LaDi)_2O_3$	2·94	162·0

The formula of the mineral appears to be $R_2O_3,2SiO_2$, in which R_2O_3 may be replaced by its equivalent in RO, RO_2, or RO_3 (Compare analysis of gadolinite in preceding abstract).

Thoro-gummite, a hydrated uranium thoro-silicate, occurs intimately associated with fergusonite and cyrtolite. It is of a dull, yellowish-brown colour, has a hardness of 4 to 4·5, and a sp. gr. of 4·43 to 4·54. The analytical results given by the authors correspond with the formula $UO_3,3ThO_2,3SiO_2,6H_2O$.

Nivenite is the name given by the authors to a hydrated thorium yttrium lead uranate found intimately associated with fergusonite and thoro-gummite. Its sp. gr. is 8·01, and its hardness 5·5. It is velvet-black, and gave on analysis—

UO_3.	UO_2.	ThO_2.	Y_2O_3.	Fe_2O_3.	PbO.	Ignition.	Insol.	Total.
46·75	19·89	7·57	11·22	0·58	10·16	2·54	1·22	99·93

The general formula is $9RO,4UO_3,3H_2O$. The mineral is allied to cleveite and bröggerite (Abstr., 1884, 1102), the relationship being as follows:—

Bröggerite..........	$3RO.UO_3$
Cleveite............	$6RO,2UO_3.3H_2O$
Nivenite	$9RO.4UO_3.3H_2O$.

The name is given in recognition of the assistance rendered by Niven in obtaining the mineral for investigation.

The heretofore rare mineral fergusonite occurs in large quantity at this new locality. The authors have found two distinct varieties. Compared with typical fergusonite, a gradation from one extreme to the other may be noted.

	Sp. Gr.	Hardness.	
Fergusonite, $R_3Nb_2O_8$	5·83	—	
Mono-hydro-fergusonite, $R_3Nb_2O_7(OH)_2$	5·67	6·5	pale olive-green, decrepitates.
Tri-hydro-fergusonite, $R_3Nb_2O_5(OH)_6$..	4·36	5·0	light brown, does not decrepitate.

Of other published analyses of fergusonite, that of the Ytterby variety by Nordenskjöld corresponds with the di-hydrated mineral.

B. H. B.

Rhodotilite and Heliophyllite from Sweden. By G. FLINK (*Jahrb. f. Min.*, 1890, i, Ref. 22—23; from *kong. Vetenskaps-Akad. Förhandl.*, 1888, 571).—1. *Rhodotilite* occurs with rhodonite, garnet, &c., at the Harstig Mine, at Pajsberg. Analysis gave the following results:—

SiO_2.	MnO.	FeO.	MgO.	CaO.	PbO.	H_2O.	Total.
43·67	37·04	1·11	0·15	9·38	0·77	7·17	99·29

This mineral is identical with the inesite of Schneider and Scheibe (this vol., p. 345 and next abstract).

2. *Heliophyllite.*—On specimens of the so-called rhodotilite from Pajsberg a yellow mineral has been observed, which resembles a mineral described by Nordenskjöld as accompanying the ekdemite of Långban. The author names this mineral heliophyllite. It gave on analysis—

PbO.	MnO,FeO.	As_2O_3.	Cl.	Total.
80·70	0·54	11·69	8·00	100·93

Its sp. gr. is 6·886, and its hardness 2. It crystallises in the rhombic system.

B. H. B.

Manganese Ores from Dillenburg. By A. SCHNEIDER (*Jahrb. f. Min.*, 1890, i, Ref. 19—22; from *Zeit. deutsch. geol. Ges.*, **39**, 829—834; *Jahrb. kgl. preuss. geol. Landesanst.*, 1888, 472—496).—An important manganese mining industry has been carried on for several years in the valley of the Scheldebach, near Dillenburg. The ore principally worked is a mixture consisting largely of klipsteinite, and containing SiO_2, Mn_2O_3, MnO, and H_2O. It is probably the result of the alteration of a manganous silicate, which still forms part of the mass. The analysis of this silicate (analysis I) approximates to

that of the stratopëite of Pajsberg. This dark amber-coloured mineral is accompanied by a dark-red ore (analysis II). Its sp. gr. is 2·675. Nests of psilomelane, manganite, and wad occur in the ore, as well as nickel-bearing iron pyrites, copper pyrites, and native copper. An anthracite is also met with. This has probably reduced the native copper, and consists of 72·67 per cent. of carbon, 3·38 per cent. of hydrogen, and 20·40 per cent. of ash-forming constituents. Anthracite is similarly met with in the neighbouring red hæmatite mines. At the contact of the manganese ore deposit with the diabase, the new mineral *inesite* (this vol., p. 345) has been met with. It is flesh-coloured, radiated, and has a hardness of 6. In composition (analysis III) inesite somewhat resembles hydrorhodonite.

	SiO_2.	Fe_2O_3.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	CO_2.	H_2O.	Total.
I.	35·64	3·02	2·59	—	39·26	1·75	1·31	0·60	13·94	98·11
II.	30·21	12·49	2·30	—	29·16	6·04	0·98	2·40	16·62	100·20
III.	43·92	—	0·29	0·69	38·23	8·00	0·28	—	8·49	99·90

B. H. B.

Theory of the Mica-group. By F. W. CLARKE (*Amer. J. Sci.*, **38**, 384—393).—Ever since its publication in 1878, Tschermak's theory of the mica-group has been in vogue, and in order to replace it by something better, two fundamental conditions must be satisfied. All micas should be reducible to one general type of formula, which should express all known relations, as do the formulæ of Tschermak, and hypothetical compounds must be as far as possible avoided. In previous papers (Abstr., 1887, 347; 1888, 117), the author has shown that all orthosilicates containing aluminium may be represented as substitution-derivatives of the normal salt $Al_4(SiO_4)_3$. He is now inclined to believe that all the true micas are referable to the same general type. The normal salts $(Al_4SiO_4)_3$ and $Al_4(Si_3O_8)_3$ are the theoretical starting points for derivation. All the micas, vermiculites, chlorites, margarite, and the clintonite-group become reducible to one general type. Representing the groups SiO_4 and Si_3O_8 by the common symbol X, the micas all fall within limits indicated by the formulæ $Al_3X_3R'_3$ and $AlX_3R'_9$. The lepidolites and other low-oxygen micas are completely accounted for on the assumption that orthosilicates and polysilicates may be isomorphously mixed; a similar state of affairs is accepted among the felspars. The author tests his formulæ by application to actual examples, taking the different micas group by group. In most cases the evidence is clear, direct, and conclusive.

B. H. B.

Allanite and Epidote as Rock-forming Minerals. By W. H. HOBBS (*Amer. J. Sci.*, **38**, 223—228).—The discovery of Cross and Iddings (Abstr., 1886, 317), that allanite occurs widely distributed as a constituent of many rocks, has called the attention of American geologists to its distinguishing characters. The author finds that two epidotic minerals occur as accessory constituents of the porphyritic granite of Ilchester, Howard Co., Maryland. These minerals exhibit interesting intergrowths. The granite in which they occur consists of large crystals of microcline scattered through a ground-mass consisting of monoclinic and triclinic felspar and biotite. Besides allanite

and epidote, the only important accessory constituent is a colourless mica. The allanite occurs as a brownish kernel within the epidote, the two minerals being crystallographically similar. It having been suggested that the surrounding mineral might not be epidote, but merely altered allanite, an analysis was made, with the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	H_2O.	P_2O_5.	Total.
37·63	(20·86)	15·29	0·31	22·93	0·31	2·23	0·44	100·00

These results correspond very closely with the formula

$$2H_2Ca_4Al_6Si_6O_{26} + H_2Ca_4Fe_6Si_6O_{26}.$$

B. H. B.

Sphærolite Tachylite from the Ussuri District. By P. N. Wenjukoff (*Jahrb. f. Min.*, 1890, i, Ref. 54—55; from *Bull. Soc. Belge géol.*, **1**, 165—176).—The rock described is somewhat similar to the hyalomelane of Sababurg. The sphærolites occur in a glassy mass with small globules filled with a granular mass, and are thought by the author to consist of a mixture of labrodorite, augite, olivine, and magnetite. The glass (analysis I). and the dark centre of the sphærolite (analysis II), gave on analysis the following results:—

	SiO_2.	Al_2O_3.	FeO.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	Total.	Sp. gr.
I.	54·19	24·40	2·72	2·04	7·85	5·70	1·72	1·85	100·47	2·51
II.	53·29	21·65	4·79	2·45	7·10	6·60	1·02	2·72	99·62	2·89

B. H. B.

Rocks used in the manufacture of Chinese Porcelain. By G. Vogt (*Compt. rend.*, **110**, 43—45).—Ebelmen and Salvetat, in 1850, concluded that the materials used in the manufacture of Chinese porcelain were very similar to those used in Europe, petun-tsé being similar in composition to the pegmatite from Limousin, although its mineralogical properties brought it into the group of compact felspars.

Yeou-ko is a variety of petun-tsé, more fusible than the latter, and used principally for the preparation of the glaze. In percentage composition it is very similar to pegmatite, but hot concentrated sulphuric acid dissolves only 3·3 per cent. of the latter, whilst it dissolves 34·15 per cent. of yeou-ko. The soluble and insoluble portions have the following composition:—

	SiO_2 hydrated.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	K_2O.
Soluble	1·01	14·20	11·28	0·46	1·14	2·97
Insoluble ..	—	62·11	2·61	—	—	0·08

	Na_2O.	CO_2.	H_2O and loss.	
Soluble	0·39	0·90	1·80	= 34·15
Insoluble	1·56	—	—	= 66·36

Almost all the sodium is in the insoluble, and almost all the potassium in the soluble portion. The insoluble portion consists of 52·95 per cent. of quartz and 13·41 per cent. of soda felspar. French pegmatite frequently contains as much as 75 per cent. of felspar. The soluble portion, neglecting the hydrated silica and the calcium

carbonate, agrees with the formula $6SiO_2,3Al_2O_3,K_2O,2\frac{1}{2}H_2O$, which is the same as that given by Tchermak for muscovite or white mica, except that it contains $\frac{1}{2}H_2O$ more.

It follows from these results that yeou-ko consists of quartz, 52·9; muscovite, 31·3; soda felspar, 13·4; calcium carbonate, 2·0; hydrated silica, 1·0 = 100·6. Pegmatite from Limousin contains—quartz, 23·87; felspar, 72·83; soluble in sulphuric acid, 3·30 = 100·00.

Muscovite occurs in all the Chinese porcelain rocks which the author has examined; petun-tsé from different localities contained the following amounts:—

	Cheo-Ki.	Yu-Khan.	Ki-Men.	Sang-Pao-Pong.
Muscovite, p. c...	40·6	37·3	31·1	18·6

Friedel and Fouqué also proved microscopically the presence of muscovite in the materials which the authors analysed. It is obvious that the presence of such large quantities of muscovite in the materials used for the making of Chinese porcelain must exert considerable influence on the product. C. H. B.

Meteorite from Carcote, Chili. By W. Will and J. Pinnow (*Ber.*, **23**, 345—353).—The chemical examination of a meteorite found at Carcote, in the Cordilleran desert, and described by v. Sandberger (this vol. p. 347), at whose request the authors undertook the quantitative analysis. The chief portion of the meteorite (about 80 per cent.) consists of a mixture of two silicates, one of which is readily decomposed by hydrochloric acid, and appears to belong to the olivine-gronp, whilst the other is insoluble in the acid, is as hard as quartz, seems to have a rectangular cleavage, and is probably a member of the diopside-group. Throughout the mass, chrome-ironstone is distributed, and also grains of an iron sulphide which cannot be distinguished from ordinary magnetic pyrites. Grains or small plates of the nickel-iron alloy are also found in considerable quantity, and a very small quantity of Rose's rhabdite. Finally, the meteorite also contains a dull, black substance of hardness 9, which consists simply of carbon in the form of black diamond. Organic matter is also present, but in unweighable quantity. The metallic constituents, the magnetic pyrites, and the decomposable silicate have been slightly weathered.

The following table gives the result of the quantitative analysis:—

	SO_3.	CaO.	MgO.	KCl,K_2SiO_3.	Cu + Sn.	Fe.	Ni + Co.	Mn.
I.	0·131	0·161	0·040	0·144	0·05	7·14	—	—
II.	—	—	—	—	—	7·28	0·74	0·12

	P.	FeS.	SiO_2.	FeO.	Al_2O_3.	MgO.	NiO + CoO.
I.	0·168	5·86	14·38	10·65	0·20	14·73	—
II.	—	—	14·59	11·29	0·21	13·93	0·43

	Mn_2O_3.	Undecomposable silicate.	Cr_2O_3,FeO.	H_2O.	C.		Total.
I.	—	40·93	1·38	1·27	0·14	=	98·85
II.	0·19	41·18	1·27	1·50	0·14	=	99·42

The composition of the portion undecomposed by hydrochloric acid is as follows :—

	SiO_2.	FeO.	Al_2O_3.	CaO.	MnO.	Na_2O.	K_2O.	Cr_2O_3,FeO.	Total.
I.	55·48	9·74	5·02	2·75	19·67	—	—	3·25	99·92
	—	—	—	—	—	3·29	0·72	1·62	

	SiO_2.	FeO.	Al_2O_3.	CaO.	MgO.	MnO.	Na_2O.	K_2O.	Cr_2O_3,FeO.	Total.
II.	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—	—	[illegible]
	—	8·83	5·06	1·85	—	—	3·31	1·27	3·00	101·05

H. . C.

Organic Chemistry.

Products of the Distillation of Coal-tar. By H. Köhler (*Dingl. polyt. J.*, **274**, 79—82).—It has been observed by Staveley that after the distillation of coal-tar is complete, an oil, consisting of light paraffins mixed with water, drops from the condenser. The same chemist has found paraffins in the receivers through which the injurious gases given off during the distillation are passed before they are burnt. The author has examined German tars with a similar purpose, but failed to detect the presence of light paraffins in the distillates referred to. The results of his investigation, however, lead him to conclude that during the distillation of coal-tar at higher temperatures dissociation of oxgenated compounds, presumably phenols, takes place, resulting in the formation of light hydrocarbons which are wholly nitratable, together with the separation of water. D. B.

Paraffin. By B. Pawlewski (*Ber.*, **23**, 327—329).—This paper gives the results of an investigation of paraffin solutions by Raoult's method. The paraffin employed was a white, ozokerite paraffin of the best quality, having a sp. gr. of 0·9170 at 20°, melting at 64—65°, and solidifying at 61—63°. It was dissolved in varying proportions of glacial acetic acid, benzene, and xylene, and the freezing points of each solution determined. From the results obtained the author draws the following conclusions:—(1) The size of the normal molecule of paraffin lies between $C_{24}H_{50}$ and $C_{27}H_{56}$; (2) it has a molecule at least double this size in dilute benzene and xylene solutions; (3) that in almost saturated solutions paraffin has a molecule at least four times the size of the normal.

It further appears that paraffin behaves towards glacial acetic acid as a crystalloïd, and towards benzene and xylene as a colloïd. A solution of 2·2 grams of paraffin in 100 grams of benzene yields, on cooling, a jelly which can support a weight of several grams. A solution of 3·53 grams of the same paraffin in 100 grams of chloroform at 25—27° gave, on cooling, a jelly which was so firm that a

weight of 300 grams did not alter its shape. Carbon bisulphide and turpentine oil behave in a similar manner. If fine shavings of paraffin are treated with ether, they fall to powder, partially dissolving at the same time, and the solution, on remaining for 12—20 hours, and cooling to 2°, deposits the paraffin in the form of swollen flocks. In all these cases no trace of crystallisation could be observed, whereas from acetic acid the paraffin separated in scales or small plates.

Similar results to the above have been obtained with other substances by Paternò (this vol., p. 105). H. G. C.

Action of Cupric Salts on Metallic Cyanides. By R. VARET (*Compt. rend.*, **110**, 147—149).—When cupric bromide (2 mols.) is added in successive small quantities to a boiling solution of mercuric cyanide (3 mols.), the liquid becomes black, cyanogen is evolved, and a lilac precipitate separates, which, when dried at 100°, has the composition $2HgCy_2,HgBr_2,Cu_2Cy_2$. If this precipitate is boiled with the mother liquor, it becomes paler in colour, and is converted into the compound $8HgCy_2,3HgBr_2,4Cu_2Cy_2$, and if this is boiled with mercuric cyanide solution, it loses still more mercuric bromide.

If the compound $2HgCy_2,HgBr_2,Cu_2Cy_2$ is boiled with a large excess of water, it gradually loses mercuric cyanide and mercuric bromide, and leaves a residue of cuprous cyanide, but a number of intermediate products of the type $2HgCy_2,HgBr_2,xCu_2Cy_2$ are formed, x being a function of the time and the proportion of water.

A dilute solution of mercuric cyanide added to excess of cupric bromide in the cold yields cyanogen and cuprous bromide. A cold solution of cupric bromide added to excess of mercuric cyanide produces a slight precipitate, and if the filtrate is cooled, it yields blue and green crystals of hydrates of the compounds $2HgCy_2,CuBr_2$ and $HgCy_2,CuBr_2$.

Cold solutions of cupric chloride and mercuric cyanide yield the compounds $2HgCy_2,CuCl_2,6H_2O$ and $HgCy_2,CuCl_2,6H_2O$. Hot solutions, when the cupric chloride is in excess, yield cyanogen and cuprous chloride; but if the mercuric cyanide is in excess, the compound $2HgCy_2,HgCl_2,Cu_2Cl_2$ is obtained, and is much more stable than the corresponding bromine compound.

When mercuric cyanide is boiled with cuprous iodide, it yields an orange precipitate of the compound Cu_2Cy_2,HgI_2, but no cyanogen is evolved. Cuprous bromide yields a pale-green mercuric cuprous bromocyanide, but cuprous chloride is without action under these conditions.

Silver cyanide, when boiled with cupric chloride solution, yields cyanogen and a green silver cuprous chlorocyanide which alters rapidly on exposure to light. Cupric bromide reacts more energetically and forms an unstable bromocyanide. Silver cyanide is, however, not affected when boiled with cupric nitrate or sulphate for several hours.

Haloïd cupric salts react with zinc cyanide, even at the ordinary temperature, but the salts of oxy-acids must be heated to 40° before the action becomes at all rapid. In both cases there is simply double decomposition with evolution of cyanogen.

It follows from these and previous results that haloïd cupric salts will decompose all other metallic cyanides, but cupric salts of oxy-acids have no action on silver and mercuric cyanides. It is probable that the two latter salts have the formulæ Ag_2Cy_2 and Hg_2Cy_4, the cyanogen radicles being united with one another as well as with the metals. C. H. B.

Action of Hydrobromic and Sulphuric Acids on Primary Alcohols. By L. NIEMILOWICZ (*Monatsh.*, **10**, 813—828).—The author finds that in the action between hydrobromic acid in aqueous solution and sulphuric acid, the amount of bromine liberated is inversely proportional to the temperature, and to a certain extent in direct proportion to the quantity of sulphuric acid present. Such a mixture of acids may be conveniently used in the direct preparation of bromine-derivatives of the paraffins, and gives a more satisfactory yield than any of the older methods. Methyl and ethyl alcohols yield only monobromides, isoamyl alcohol gives no dibromide, but isobutyl, normal butyl, and normal propyl alcohols give mono-, di-, and tri-brominated derivatives when treated with a mixture of the acids. Alcohols which contain the isopropyl-group are much more readily attacked by the sulphuric acid mixture, and more readily form tribrominated derivatives than the normal alcohols. All the higher primary alcohols give a maximum yield of the dibrominated derivatives when heated with a mixture of the acids to a certain calculable temperature, which for propyl alcohol is 60°, for normal butyl alcohol, 50°, for isobutyl alcohol, 40°, for isoamyl alcohol, 30°, and so on. G. T. M.

Compound of Calcium Chloride with Normal Propyl Alcohol. By C. GÖTTIG (*Ber.*, **23**, 181—182).—When commercial propyl alcohol is frequently shaken with calcium chloride, allowed to remain for some time, and then distilled, the residue in the distillation flask on cooling deposits two different substances; that which forms the lower layer is quite opaque and consists of calcium chloride, alcohol, and water; whilst the second is a transparent layer of needle-shaped crystals. These are a compound of calcium chloride with normal propyl alcohol, which, when dried, have the composition $CaCl_2 + C_3H_8O$, and may be recrystallised from dry propyl alcohol without undergoing any change in composition. The compound has almost the same specific gravity as water; small, loosely aggregated pieces float on the surface, rotating in the same manner as the compounds of the alkalis with ethyl alcohol (Abstr., 1887, 550, 636; 1888, 437, 933), and dissolving slowly with liberation of propyl alcohol. It takes up water when exposed to the air, and loses 50 per cent. of its weight over sulphuric acid in a vacuum, leaving an opaque residue, which no longer rotates on the surface of water.

H. G. C.

Cryoscopic Behaviour of the Aqueous Solutions of the Sugars obtained synthetically from Formaldehyde. By N. KLOBUKOFF (*Zeit. physikal. Chem.*, **5**, 28—30).—Two preparations obtained by the condensation of formaldehyde in alkaline solution, the one containing about 85 per cent. of formose, and the other

20—21 per cent. of methose, were examined. Both gave reductions corresponding with the molecular weight 180, and therefore to the molecule $C_6H_{12}O_6$. H. C.

Synthesis of Mannose, Dextrose, and Levulose. By E. Fischer (*Ber.*, **23**, 370—394; 799—805).—The lactone of mannonic acid (Fischer and Hirschberger, this vol., p. 225) so closely resembles the lactone of arabinosecarboxylic acid (Kiliani, Abstr., 1887, 230) in properties, that the compounds would be regarded as identical were it not for the difference in optical activity, the former having a specific rotation of $[\alpha]_D = 53\cdot81$, the latter of $[\alpha]_D = - 54\cdot8$. When mixed in equal proportions, the two substances yield an optically inactive lactone which can only be separated into its optically active constituents by special methods (*vide infra*); it is therefore evident that the two lactones are optically active isomerides of opposite rotatory power. On reduction with sodium-amalgam (compare Fischer, Abstr., 1889, 1149), the three lactones yield the corresponding glucoses and mannitols. In view of the fact that the rotation of derivatives of each isomeride is not always in the same direction—for example, the hydrazones and osazones of dextro-rotatory mannose are lævo-rotatory and *vice versâ*—it is necessary to adopt some method of indicating the optical activity of the parent glucose, and the author proposes to distinguish the derivatives of dextro- and lævo-rotatory, and of inactive mannose, irrespective of their own peculiar rotation, as derivatives of d.-, l.-, and i.-mannose respectively.

l.-Mannose (lævo-rotatory mannose) is obtained when 1 part of the lactone of arabinosecarboxylic acid dissolved in 10 parts of water slightly acidified with sulphuric acid and cooled in a freezing mixture, is treated with 2½ per cent. sodium-amalgam, added in small quantities at a time with continual shaking, the solution being always kept slightly acid; hydrogen begins to make its appearance when about 15 parts of the amalgam and 1·3 parts of 20 per cent. sulphuric acid have been employed, and the reduction is complete when 2 drops of the solution completely reduce 15 drops of Fehling's solution. The product is carefully neutralised, concentrated to crystallising point, and systematically extracted with boiling alcohol in order to separate the mannose from sodium sulphate and any unattacked sodium arabinosecarboxylate; the mannose is then obtained as a syrup by the evaporation of the alcoholic solution. The yield amounts to about 50 per cent. of the theoretical. l.-Mannose is readily soluble in water, tolerably soluble in methyl alcohol, and sparingly soluble in absolute alcohol. It is lævo-rotatory, but the specific rotation could not be determined owing to lack of material. Fermentation with yeast takes place very slowly, if at all, in 5 per cent. aqueous solution, and the greater part of the mannose is found to be unaltered after 12 days' contact with the ferment. *l.-Mannosephenylhydrazone*, $C_{12}H_{18}N_2O_5$, forms slender, colourless crystals, melts, when rapidly heated, at about 195° with the evolution of gas, can be crystallised from 40 parts of boiling water, and is therefore more soluble in hot water than d.-mannosephenylhydrazone, and is dextrorotatory in hydrochloric acid solution. *l.-Mannosephenylglucosazone*,

$C_{18}H_{22}N_2O_4$, crystallises in slender, yellow needles, becomes dark, when rapidly heated, at about 195°, and melts at about 205°; its properties closely resemble those of ordinary d.-phenylglucosazone, obtained from d.-mannose, dextrose, or levulose, but it is strongly dextro-rotatory in acetic acid solution. On treatment with concentrated hydrochloric acid, it is converted into the corresponding osone, which will unquestionably yield dextro-rotatory levulose (l.-levulose, *vide infra*) on reduction with zinc-dust and acetic acid.

l.-Mannitol.—The reduction of l.-mannose to l.-mannitol, which takes place much more slowly than the reduction of the lactone, is best effected by adding small quantities of $2\frac{1}{2}$ per cent. sodium-amalgam to a 10 per cent. aqueous solution, neutralising the alkali between each addition, and continuing the operation until 3 drops of the solution no longer reduce 1 drop of Fehling's solution; the l.-mannitol is then extracted with alcohol by the method described under l.-mannose. It crystallises from water in slender needles, from methyl alcohol in spherical aggregates of needles, melts at 163—164°, is readily soluble in water, tolerably soluble in hot methyl alcohol, and sparingly soluble in absolute alcohol, has a sweet taste, does not reduce Fehling's solution, and is strongly lævo-rotatory in the presence of borax. The mannitol obtained by Kiliani by the reduction of the double lactone of metasaccharic acid (Abstr., 1888, 46), is in all probability identical with l.-mannitol.

i.-Mannonic acid is formed by dissolving equal parts of the lactones of d.-mannonic acid and arabinosecarboxylic acid in water. It crystallises in stellate groups of long, lustrous prisms, sinters at 149°, melts at 155°, has a sweet taste, and does not reduce Fehling's solution. It is readily soluble in water, sparingly soluble in alcohol, and is optically inactive even in a 25 per cent. solution. The *calcium* salt, $(C_6H_{11}O_7)_2Ca$, is anhydrous, and crystallises in spherical aggregates of slender needles; the crystallised salt requires 60—70 parts of boiling water for its solution, and in aqueous solution is optically inactive. The *phenylhydrazide*, $C_{12}H_{18}N_2O_6$, crystallises from water in small, lustrous, seemingly cubical forms, melts, when rapidly heated, at 230° with the evolution of gas, and is less soluble in water than the corresponding derivatives of d.-mannonic and arabinosecarboxylic acids. i.-Mannonic acid cannot be separated into its optically active components by crystallisation, and to effect this, recourse must be had to Pasteur's methods. Fermentation of the neutral ammonium i.-mannonate with *Penicillium glaucum* in a nutritive solution did not give satisfactory results, in spite of a rich growth of mycelium and occurrence of fructification, since at the end of three weeks, when further growth ceased, the solution was lævo-rotatory only to the extent of 1°. Crystallisation of the sparingly soluble strychnine salt, however, gave the desired separation. The strychnine salt was prepared by heating the i.-lactone with strychnine in molecular proportion, in 70 per cent. alcohol, for a considerable time and concentrating the alcoholic solution, whereby about 12 per cent. of the strychnine separated, whilst the corresponding amount of the lactone remained in solution; by further evaporation, the strychnine salt separated as a crystalline mass consisting of slender needles, and was

freed from adhering lactone by repeated washing with alcohol. When warmed with absolute alcohol, the salt at first dissolves forming a clear solution; but in a very short time the very sparingly soluble strychnine arabinosecarboxylate crystallises out from the boiling solution, and can be purified by extraction with boiling alcohol. The salt insoluble in alcohol, amounting to about one-third of the salt of the inactive acid employed, is pure strychnine arabinosecarboxylate, and by decomposition with baryta-water and acidification with sulphuric acid, yields the corresponding lactone melting at 146—151°. The alcoholic mother liquor obtained after the separation of the strychnine arabinosecarboxylate contains chiefly strychnine d.-mannonate, together with some of the former salt; and when cooled at 0° gives a separation of the two in about equal proportions in slender, lustrous crystals amounting to about half of the salt of the inactive acid employed. A portion of the arabinosecarboxylate is removed by extracting the crystalline separation with hot alcohol, and the remainder is separated by converting the strychnine salt into the morphine salt, and crystallising the sparingly soluble morphine d.-mannonate first from water, and finally from methyl alcohol. When decomposed with baryta-water, and subsequently neutralised with dilute sulphuric acid, it is converted into the corresponding d.-lactone. The process can be reversed and the d.-lactone separated first from the i.-lactone by means of the morphine salt; the l.-lactone is then purified by conversion into the strychnine salt.

i.-Mannose is obtained by the reduction of the lactone of i.-mannonic acid by the method already described under l.-mannose. It is a colourless syrup, which is readily soluble in water, tolerably soluble in hot methyl alcohol, sparingly soluble in absolute alcohol, and, apart from its optical inactivity, has all the properties of d.- and l.-mannose. On fermentation with yeast, the solution becomes lævorotatory in consequence of the rapid decomposition of the dextrorotatory component, l.-mannose being only slowly acted on by the ferment. The *i.-phenylhydrazone*, $C_{12}H_{18}N_2O_5$, is sparingly soluble, melts at about 195° with decomposition, and is optically inactive; the *i.-phenylglucosazone*, $C_{18}H_{22}N_4O_4$, crystallises in slender, lustrous, yellow needles, becomes dark at about 210°, melts at 217—218° with decomposition, is soluble in about 250 parts of boiling alcohol, is optically inactive in acetic acid solution, and has all the properties of α-acrosazone, with which the author regards it as identical. α-Acrosazone will therefore be referred to in future as i.-phenylglucosazone.

i.-Phenylglucosazone (α-acrosazone) and i.-mannitol (α-acritol) are obtained from α-acrose, and it follows therefore that this synthetical glucose must either be i.-levulose or i.-mannose, since these carbohydrates are the only two which could yield the same optically inactive osazone and mannitol. Unlike i.-mannose, α-acrose does not yield a phenylhydrazone; it must, therefore, be i.-levulose, and its production from acraldehyde bromide must be referred to the simultaneous formation of glyceraldehyde and the isomeric symmetrical dihydroxyacetone, which then undergo condensation, thus:—

$$CH_2(OH)\cdot CH(OH)\cdot COH + CH_2(OH)\cdot CO\cdot CH_2(OH) = \\ CH_2(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CO\cdot CH_2(OH).$$

On fermentation with yeast, α-acrose is separated into its optically active constituents; the d.-levulose (ordinary lævo-rotatory levulose) is removed, and the solution becomes dextro-rotatory. The l.-levulose (that is, the dextro-rotatory modification) could not be isolated on account of the small quantity at disposal, but reacts like ordinary levulose (d.-levulose) in forming an osazone identical with l.-phenylglucosazone, but no hydrazone.

i.-Mannitol is obtained from i.-mannose by the reduction method employed in the preparation of l.-mannitol; the yield amounts to about 40 per cent. of the theoretical. It crystallises in small prisms, melts at 168° (at 170° corr.), is readily soluble in water, tolerably soluble in hot acetic acid, and very sparingly soluble in methyl and ethyl alcohol, is optically inactive, and identical with α-acritol. The name i.-mannitol will therefore be employed for both compounds. On oxidation with dilute nitric acid, i.-mannitol yields about 20 per cent. of i.-mannose, and this, by oxidation with bromine, is converted into i.-mannonic acid, which can be isolated by means of its phenylhydrazide by the method already described (Fischer and Hirschberger, *loc. cit.*); it is therefore possible to prepare synthetically all carbohydrates of the mannose and levulose series.

The synthesis of dextrose from d.-mannonic acid, and therefore from α-acrose, is described in the second paper (*Ber.*, **23**, 799—805), in which it is shown that d.-mannonic acid can be partially converted into gluconic acid, and *vice versâ*, by heating it with twice its weight of quinoline at 140° for 40 minutes; the product from either source containing about 40 per cent. of d.-mannonic acid and 60 per cent. of gluconic acid. To separate these acids, the product obtained by heating d.-mannonic acid (20 grams) with quinoline (40 grams) and water (5 grams) at 140° for 40 minutes is treated with a solution of barium hydroxide (40 grams), steam-distilled to remove all quinoline, exactly neutralised by sulphuric acid, and concentrated to 150 c.c. It is then heated with brucine (60 grams) until dissolved, allowed to remain in the cold for some time in order to remove all excess of brucine by crystallisation, then concentrated to the crystallising point, dissolved in 25 times its volume of boiling absolute alcohol, and the brucine d.-mannonate, which is only sparingly soluble in absolute alcohol, separated by crystallisation. The alcoholic filtrate from this is evaporated to a syrup, which is dissolved in water, treated with a solution of barium hydroxide (20 grams) to liberate the brucine, and the filtrate carefully precipitated with sulphuric acid. The clear solution is now concentrated to 30 c.c., and heated at 100° for an hour with phenylhydrazine (3 grams) in the form of acetate, in order to convert the gluconic acid into its phenylhydrazide, which crystallises out on cooling, and can be reconverted into the acid by the method already described (Fischer and Hirschberger, *loc. cit.*). Gluconic acid, so prepared, has all the properties of ordinary gluconic acid.

To obtain dextrose from gluconic acid, the aqueous solution is evaporated to a thick syrup on the water-bath, with the object of forming as much lactone as possible, and then reduced by adding sodium-amalgam to the cold 10 per cent. aqueous solution in the way already described. The yield is not so good as that obtained when any of the

α-acrose [prepared from acraldehyde bromide (Abstr., 1888, 40), glycerose (Abstr., 1888, 358), or formaldehyde (Abstr., 1889, 483)]
[by heating with phenylhydrazine acetate (Abstr., 1889, 483)]
i.-phenylglucosazone
[by treatment with concentrated hydrochloric acid (Abstr., 1888, 1267)]
i.-glucosone
[by reduction with zinc-dust and acetic acid (Abstr., 1889, 485)]
i.-levulose
[by fermentation with yeast] [by reduction with sodium-amalgam]

l.-levulose (dextro-rotatory)
l.-phenylglucosazone

i.-mannitol (α-acritol)
[by oxidation with nitric acid]
i.-mannose
[by oxidation with bromine]
i.-mannonic acid
[by separation with strychnine and morphine]

l.-mannonic acid [arabinosecarboxylic acid (lævo-rotatory)]
[by reduction with sodium-amalgam]
l.-mannose
[by further reduction]
l.-mannitol

d.-mannonic acid (dextro-rotatory)
[by reduction with sodium-amalgam] [by heating with quinoline]

d.-mannose
[by further reduction] [by treatment with phenylhydrazine acetate]
d.-mannitol
d.-phenylglucosazone
[by reduction (Abstr., 1889, 484)]
d.-glucosone
[by reduction]
isoglucosamine
[by nitrous acid]
d.-levulose (ordinary lævo-rotatory levulose).

gluconic acid
[by reduction]
d.-dextrose (ordinary dextro-rotatory dextrose)

three mannonic acids are reduced; this is due in all probability to the fact that gluconic acid is only incompletely converted into its lactone, since the property of undergoing reduction by sodium-amalgam is seemingly intimately associated with that of forming lactones in acids of this class. The synthetical dextrose has a specific rotatory power of $[\alpha]_D = 52$, yields d.-phenylglucosazone, and is identical with ordinary dextrose. It follows therefore that, with the exception of l.-gluconic acid, which the author is attempting to prepare from l.-mannonic acid (arabinosecarboxylic acid) by heating with quinoline, l.-dextrose, and the optically inactive forms of these compounds, all the carbohydrates of the mannitol series have been prepared synthetically; the relation of these carbohydrates to α-acrose is shown in the table (p. 470).

W. P. W.

Matezite and Matezo-dambose. By C. COMBES (*Compt. rend.*, **110**, 46—47).—Girard (*Compt. rend.*, **77**, 995) obtained from Madagascar caoutchouc, a saccharine substance, matezite, which, when treated with hydriodic acid, yields methyl iodide and matezo-dambose, an isomeride of glucose. β-Pinite, obtained by Maquenne from *Pinus lambertiana*, behaves in a similar manner, and with hydriodic acid yields methyl iodide and β-inosite (this vol., p. 244). Matezite and β-pinite both crystallise in radiating nodules, and matezo-dambose and β-inosite are precipitated in tetrahedra on addition of alcohol to their aqueous solutions. Both the latter give Scherer's reaction, and have a molecular weight of 171 as determined by Raoult's method. These facts and the following measurements show that β-pinite and β-inosite are not distinct chemical species, but are identical with matezite and matezo-dambose respectively.

	Matezite.	β-pinite.	Matezo-dambose.	β-inosite.
Melting-point ..	187°	186·5°	246°	246°
Rotatory power.	66·0°	65·7°	67·6°	68·4°

C. H. B.

Rotatory Power of Matezite and Matezo-dambose. By A. GIRARD (*Compt. rend.*, **100**, 84—86).—The value of the rotatory power given in an earlier paper was erroneous, and the author has recalculated the numbers from his old data—

Matezite $[\alpha]_D = +\ 65·2°$. Matezo-dambose $[\alpha]_D = +\ 65·4°$.

New determinations give very similar results.

Matezite $[\alpha]_D = +\ 64·7°$. Matezo-dambose $[\alpha]_D = +\ 64·7°$.

The rotatory-powers are therefore identical, and not different as was formerly supposed (compare Combes, preceding abstract).

C. H. B.

Racemo-inosite. By MAQUENNE and C. TANRET (*Compt. rend.*, **110**, 86—88).—Inosite from quebrachite is lævogyrate, and inosite from pinite dextrogyrate, their rotatory powers being exactly equal, but of opposite sign. For the hydrated compounds, $[\alpha]_D = \pm\ 65°$; and for the anhydrous, $[\alpha]_D = \pm\ 55°$. Both soften without decomposing above 210°, and melt at 247°; both crystallise in hemihedral rhomboidal prisms, give the same reactions, and have the same solu-

bilities both in the hydrated and anhydrous forms. Their acetates soften in the hand, and have equal but opposite rotatory powers (10°); the benzoates crystallise in comparatively insoluble, brilliant needles which melt at 252°.

When solutions of equal quantities of the two inosites are mixed, an abundant crystalline precipitate of *racemo-inosite* is obtained. It is optically inactive, melts at 253° without softening, is much less soluble than the active varieties, and separates from solution only in the anhydrous form. It does not affect Fehling's solution in the cold. The acetate is crystalline and melts at 111°, and the benzoate forms bulky, microscopic needles which melt at 217°.

Racemo-inosite has the same composition as the active inosite, to which it stands in the same relation as racemic acid does to the active tartaric acids. It is the first example of physical isomerism amongst the sugars. C. H. B.

Xylose and Wood-gum from Straw and other Materials. By E. W. Allen and B. Tollens (*Ber.*, **23**, 137).—When loofah, straw, or cherry-wood is extracted with soda, and the extract mixed with alcohol, a gum is precipitated; in the case of straw, the yield of crude gum is 16 per cent., and, on hydrolysis, it gives xylose.

F. S. K.

Derivatives of Propylamine. By S. Gabriel and W. E. Lauer (*Ber.*, **23**, 87—96).—Continuing Gabriel's previous work on the derivatives of fatty amines, the authors have investigated some more of the derivatives of propylamine.

When γ-bromopropylphthalimide (Abstr., 1888, 1292) is digested with potash, the potassium salt of *hydroxypropylphthalamic acid* is formed. If the syrupy acid is heated for 3—4 hours at 135—145°, water is separated, and *γ-hydroxypropylphthalimide*,

$$C_8H_4O_2:N\cdot C_3H_6\cdot OH,$$

is produced. This crystallises from water in colourless needles.

Propylmercaptophthalimide, $C_8H_4O_2:N\cdot C_3H_6\cdot SH$, is formed when bromopropylphthalimide is heated with alcoholic potassium hydrosulphide in sealed tubes at 100°. It is soluble in alcohol and light petroleum, insoluble in water, crystallises in colourless needles, and melts at 46—48°. When heated with fuming hydrochloric acid, it decomposes into phthalic acid and γ-amidopropylmercaptol.

γ-Thiocyanopropylphthalimide, $C_8H_4O_2:N\cdot C_3H_6\cdot SCN$, is formed when bromopropylphthalimide is heated with alcoholic potassium thiocyanate at 100°. It crystallises from alcohol in colourless needles melting at 96—98°. When this compound is digested with potash, it yields *dipropyldisulphide-γ-diphthalamic acid*, $S_2(C_3H_6\cdot NH\cdot CO\cdot C_6H_4\cdot COOH)_2$; this crystallises in colourless scales melting at 136°, is soluble in glacial acetic acid, ammonia, and alkalis, insoluble in water. When digested with concentrated hydrochloric acid at 200°, it is decomposed into phthalic acid and *dipropylamido-γ-disulphide hydrochloride*,

$$S_2(C_3H_6\cdot NH_2)_2,2HCl,$$

which crystallises in white needles melting at 218—219°, and yields

a sparingly soluble picrate, $C_6H_{16}N_2S_2,2C_6H_2(NO_2)_3\cdot OH$, which crystallises from alcohol in yellow scales melting at 145—146°.

γ-Amidopropyl hydrogen sulphate, $NH_2\cdot C_3H_6\cdot O\cdot SO_3H$, is formed when γ-bromopropylamine hydrobromide is added to a hot aqueous solution of silver sulphate. It forms crystals, soluble in hot water, and melting at 221°.

μ-Mercaptopenthiazoline, $CH_2<\substack{CH_2\cdot S\\ CH_2\cdot N}\geqslant C\cdot SH$, is formed by the action of carbon bisulphide on γ-bromopropylamine hydrobromide. It is easily soluble in hot water and alcohol, insoluble in acids, forms colourless crystals, and melts at 132°. When oxidised by heating with bromine-water, this compound yields *γ-amidopropylsulphonic acid*, $NH_2\cdot C_3H_6\cdot SO_3H$, which crystallises from alcohol in needles, and does not melt below 300°. This acid is isomeric with β- and ν-methyltaurine. The mother liquors from this acid contain a less oxidised derivative of the thiazoline, which forms fibrous crystals, very soluble in water.

Trimethylene-ψ-thiocarbamide, $CH_2<\substack{CH_2-S\\ CH_2\cdot NH}>C\colon NH$, is formed by the action of potassium thiocyanate on γ-bromopropylamine hydrobromide. It is a strongly-smelling oil, with strong alkaline reaction, and is less stable than the corresponding ethylene-derivative. Its *hydrobromide*, $C_4H_9N_2SBr$, is soluble in water, and forms crystals melting at 135—136°; its *picrate* forms long needles melting at 128°.

Trimethylene-ψ-carbamide, $CH_2<\substack{CH_2-O\\ CH_2\cdot NH}>C\colon NH$, is formed when potassium cyanate is substituted for thiocyanate in the above reaction. It is a thick, strongly basic oil, yielding a *picrate*, crystallising in yellow needles, and melting at 200°. L. T. T.

New Hexylamine and a New Hexyl Alcohol. By M. FREUND and P. HERRMANN (*Ber.*, **23**, 189—196).—The starting point for these compounds is diethylacetic acid, obtained by Conrad's method from ethyl malonate: for every 100 grams of the latter employed, 25 grams of diethylacetic acid was obtained.

Diethylacetic chloride, $CHEt_2\cdot COCl$, is obtained by acting on the acid with phosphorus trichloride at the ordinary temperature, and then carefully distilling. It is a fuming liquid, having a pungent odour, and boiling at 134—137°. It readily acts on sodium diethylacetate, forming *diethylacetic anhydride*, $O(CO\cdot CHEt_2)_2$, a colourless liquid, which has a faint odour, and boils at 230°.

Diethylacetamide, $CHEt_2\cdot CO\cdot NH_2$, is prepared by passing ammonia gas into the free acid, and heating the ammonium salt thus obtained in a sealed tube at 240—250° for 5—6 hours. It crystallises from absolute alcohol in long needles which melt at 105°, boils without decomposition at 230—235°, and is readily soluble in water, alcohol, and ether.

Diethylacetanilide, $CHEt_2\cdot CO\cdot NHPh$, is obtained from the foregoing compound by boiling it with aniline and a little hydrochloric acid. It crystallises from alcohol in slender needles which melt at 124°, and are almost insoluble in water.

Diethylacetonitril, $CHEt_2{\cdot}CN$, is formed when the amide is mixed with phosphorus pentoxide and carefully distilled. It is a somewhat volatile liquid of pleasant odour, boils at 144—146°, and mixes with alcohol and ether, but is almost insoluble in water.

β-Diethylethylamine hydrochloride, or *pseudohexylamine hydrochloride*, $CHEt_2{\cdot}CH_2{\cdot}NH_2,HCl$, is prepared by adding sodium to a boiling alcoholic solution of diethylacetonitril, and distilling the liquid formed in a current of steam. The distillate is collected in hydrochloric acid, the solution evaporated to dryness, and any ammonium chloride present removed by digestion with absolute alcohol. On evaporation, the filtered solution leaves pseudohexylamine hydrochloride as a white, somewhat hygroscopic powder. It crystallises from alcohol containing a little ether or light petroleum in a network of fine needles, melting with decomposition at 187°, and very readily soluble in water and alcohol. The *platinochloride*, $(CHEt_2{\cdot}CH_2{\cdot}NH_2)_2,H_2PtCl_6$, is very insoluble, and forms golden-yellow, brilliant scales.

The free base is obtained by adding a slight excess of concentrated potash solution to the hydrochloride suspended in ether, drying the ethereal solution over solid caustic potash, and distilling. *Pseudohexylamine* is a liquid of ammoniacal odour, which boils at 125·3° (corr.), and rapidly absorbs carbonic anhydride from the air.

Pseudohexylcarbamide, $NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CHEt_2$, is prepared by evaporating a solution of equal weights of pseudohexylamine hydrochloride and potassium cyanate; from the potassium chloride also formed, it is separated by digesting with absolute alcohol, evaporating the solution, washing with a little water, and recrystallising several times from hot water. It forms small plates which melt at 116·5°, and are sparingly soluble in cold, readily in hot water or alcohol.

Pseudodihexyloxamide, $C_2O_2(NH{\cdot}CH_2{\cdot}CHEt_2)_2$, is formed by warming pseudohexylamine and oxamide in ethereal solution. It crystallises from alcohol in beautiful needles melting at 144°.

Symmetrical phenylpseudohexylcarbamide, $NHPh{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CHEt_2$, and *symmetrical phenylpseudohexylthiocarbamide*,

$$NHPh{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}CHEt_2,$$

are obtained when a solution of pseudohexylamine in absolute alcohol is heated with phenyl cyanate and phenylthiocarbimide respectively. The former crystallises in fascicular groups of needles, and melts at 70°, whereas the latter separates from solution as an oil, but may be obtained in the crystalline state by precipitating its alcoholic solution with water, adding a solid particle, and scratching with a glass rod. After repeating this process several times, it crystallises in small prisms which melt at 52—53°, and still contain traces of phenylthiocarbamide.

Pseudohexyl alcohol, $CHEt_2{\cdot}CH_2{\cdot}OH$.—To prepare this alcohol, pseudohexylamine hydrochloride is digested with an excess of silver nitrite and a little water, and the filtrate distilled. The alcohol swims on the aqueous distillate as a yellow oil, and is freed from traces of the amine by hydrochloric acid, dried over ignited potassium carbonate, and finally over baryta, and fractionated. It is a colour-

less liquid, having an odour resembling that of camphor and of fusel oil, and boils at 139—143°. Between the boiling-points of the alcohol and the acid there is, therefore, approximately the same difference as between the other known hexyl alcohols and the corresponding acids.

H. G. C.

Derivatives of Ammonium Chloride. By J. A. LE BEL (*Compt. rend.*, **110**, 144—147).—If it is admitted that the atoms or radicles in a substituted ammonia are capable of movement round the central nitrogen-atom, and have not fixed and definite relative positions, it is possible to imagine the existence of two isomeric derivatives, without assuming that they have been formed in different ways, as for example by the union of RCl with NR'_3, or R'Cl with NRR'_2.

Amongst the platinochlorides of the amines there is a remarkable group of cubic salts, formed from chlorides of the type NRR'_3Cl. To this group belong methyltripropylammonium platinochloride and trimethylpropylammonium platinochloride, but the limit is passed by the trimethylisobutylammoninm salt. As a rule, if a platinochloride does not differ from the cubic salts by more than a single methyl-group, its crystalline form will be so nearly a cube that very careful goniometric and optical examination will be necessary to prove that it is not cubic.

Trimethylisobutylammonium platinochloride was first obtained in highly birefractive needles, distinctly not cubic, but when these were recrystallised in order to obtain larger crystals, octohedra were obtained very closely resembling regular octohedra, and their character was not altered by recrystallisation. All attempts to reconvert the octohedral platinochloride into the prismatic form failed, but when the salt was agitated with pure precipitated silver oxide, the platinum and chlorine were precipitated together, and if the compound ammonia in the filtrate was neutralised with hydrochloric acid and concentrated rapidly in a vacuum, the hydrochloride was obtained partly in needles and partly in octohedra. It follows that there are not only two platinochlorides, but two hydrochlorides, the prismatic hydrochloride being more stable than the corresponding platinochloride. The octohedral hydrochloride changes into the prismatic form in presence of excess of the original hydrochloride, especially if a little free acid is present.

C. H. B.

Action of Ammonia and of Ethylenediamine on Tetrachlorodiacetyl. By S. LEVY (*Annalen*, **254**, 374—376).—The compound (m. p. 127°) obtained by treating tetrachlorodiacetyl with ammonia (this vol., p. 233) is identical with the amide of trichloropropyleneoxidecarboxylic acid obtained from tetrachloracetone; probably it has the constitution $\begin{matrix} ClHC \\ | \\ O \end{matrix}\!>C(CONH_2)\cdot CHCl_2$.

If such is the case, the compound obtained from tetrachlorodiacetyl and ethylenediamine probably has the constitution

$$\begin{matrix} ClHC \\ | \\ O \end{matrix}\!>C(CHCl_2)\cdot CO\cdot NH\cdot C_2H_4\cdot NH\cdot CO\cdot C(CHCl_2)<\!\begin{matrix} CHCl \\ | \\ O \end{matrix}.$$

F. S. K.

Diethylenediamine. By J. Sieber (*Ber.*, **23**, 326—327).—Diethylenediamine is formed when ethylenediamine is treated with ethylene bromide; the product is decomposed with potash, the resulting oil dried, fractionated, and the portion passing over at 168—175° collected separately. The base could not be obtained in an anhydrous condition. The *hydrochloride*, $C_4H_{10}N_2,2HCl$, crystallises in small, colourless needles, and is readily soluble in water, but insoluble in alcohol. The *platinochloride*, $C_4H_{10}N_2,H_2PtCl_6$, crystallises in small, yellow needles, and is moderately easily soluble in hot water, but only very sparingly in hot alcohol. The *mercurochloride*, $C_4H_{10}N_2,H_2HgCl_4$, crystallises in concentrically grouped needles, and is readily soluble in hot water, but is reprecipitated on adding alcohol. The *picrate*, $C_4H_{10}N_2,C_6H_3N_3O_7$, crystallises from water in yellow needles, and is almost insoluble in alcohol. F. S. K.

Propylthiocarbimide and some New Thiocarbamides. By O. Hecht (*Ber.*, **23**, 281—288).—*Propylammonium propyldithiocarbamate* separates in colourless crystals, when normal propylamine is mixed with ether and treated in the cold with the theoretical quantity of carbon bisulphide. It is readily soluble in water and alcohol, and melts at 102° with decomposition.

Propylthiocarbimide, NPr:CS, is obtained when the preceding compound is dissolved in alcohol, the solution shaken with a concentrated aqueous solution of mercuric chloride, and then distilled with steam. The yield is 42 per cent. of the theoretical quantity. It is a colourless, highly refractive liquid, with a strong odour of mustard oil; it boils at 152·7° (743 mm.), has a sp. gr. of 0·9304 at 99·4°, (water at 99·4° = 1) and is only sparingly soluble in water, but miscible with alcohol, ether, acetone, benzene, chloroform, and light petroleum.

Propylthiocarbamide, $NHPr{\cdot}CS{\cdot}NH_2$, prepared by dissolving propylthiocarbimide in ammonia, separates from alcohol in colourless, quadratic plates, melts at 110°, and is moderately easily soluble in water. The *methyl*-derivative, NHPr·CS·NHMe, prepared by treating propylthiocarbimide with methylamine, or by treating methylthiocarbimide with propylamine in alcoholic solution, crystallises in colourless plates, melts at 79°, and is very easily soluble in alcohol, acetone, and chloroform, and readily in ether, benzene, and carbon bisulphide, but only sparingly in water and light petroleum. The *ethyl*-derivative, NHPr·CS·NHEt, crystallises in small, colourless plates, and melts at 52°; it is moderately easily soluble in water, and behaves like the corresponding methyl-derivative with other solvents. The *propyl*-derivative, $CS(NHPr)_2$, crystallises in colourless, nacreous plates, melts at 71°, and is only sparingly soluble in cold, but moderately easily in hot, water.

Dipropylcarbamide, $CO(NHPr)_2$, prepared by treating an alcoholic solution of the thiocarbamide with mercuric oxide, crystallises from hot water in needles, and melts at 105°.

Propylallylthiocarbamide, $NHPr{\cdot}CS{\cdot}NH{\cdot}C_3H_5$, can be obtained by treating propylthiocarbimide with allylamine, or by treating allylthiocarbimide with propylamine; it crystallises in large, transparent

plates, melts at 60°, and is only very sparingly soluble in cold, but moderately easily in hot, water.

Propylphenylthiocarbamide, NHPr·CS·NHPh, crystallises from alcohol in colourless, nacreous plates, melts at 63°, and is only sparingly soluble in hot water.

Dimethylthiocarbamide, $CS(NHMe)_2$, is a colourless, crystalline compound melting at 51·5°; it is very readily soluble in alcohol, chloroform, and acetone, but only sparingly in ether, benzene, carbon bisulphide, and light petroleum.

Methylallylthiocarbamide, $NHMe{\cdot}CS{\cdot}NH{\cdot}C_3H_5$, is a colourless, crystalline compound melting at 52°; *ethylallylthiocarbamide* forms large, transparent crystals, and melts at 47°.

Diallylthiocarbamide, $CS(NH{\cdot}C_3H_5)_2$, crystallises in large, transparent plates, and melts at 49·5°. F. S. K.

Thioaldehydes. By E. BAUMANN (*Ber.*, **23**, 60—69).—Baumann and Fromm showed (this vol., p. 25) that when acetaldehyde is treated with hydrogen sulphide in the presence of hydrochloric acid, two isomeric trithioaldehydes are formed, and that benzaldehyde in like manner yields two isomeric thiobenzaldehydes. The author has tried the same reaction with formaldehyde, but in all cases the trithioformaldehyde, $C_3H_6S_3$, described by Hofmann (*Annalen*, **145**, 357) was alone produced. As this compound is also formed in so many other ways, and as no isomeride of it has been obtained, there can be little doubt that the peculiar isomerism occurring with the higher members of this class does not extend to the simplest member thereof.

In text-books it is stated that trithioformaldehyde is formed when hydrogen sulphide is passed into a solution of formaldehyde. This is not the case; this and the homologous aldehydes only being formed in the presence of strong acids or dehydrating agents. The first action of hydrogen sulphide on aldehydes seems to be the formation of a compound SH·R·OH, two or more molecules of which then unite with separation of water and formation of more or less complicated compounds of a mercaptan-like character, the reactions being probably represented by the equations—

$$2SH{\cdot}R{\cdot}OH = SH{\cdot}R{\cdot}O{\cdot}R{\cdot}SH + H_2O;$$
$$2SH{\cdot}R{\cdot}OH = SH{\cdot}R{\cdot}S{\cdot}R{\cdot}OH + H_2O;$$
$$SH{\cdot}R{\cdot}OH + OH{\cdot}R{\cdot}OH = OH{\cdot}R{\cdot}S{\cdot}R{\cdot}OH + H_2O;$$

and so on. These compounds are very difficult to isolate, and under the influence of hydrochloric acid, &c., are converted into trithioaldehydes. With formaldehyde, the intermediate products were obtained as a semi-crystalline mass easily soluble in caustic soda solution, from which it was reprecipitated by acids. Its alcoholic solution gives with lead salts a bright yellow precipitate, which on heating yields lead sulphide. By passing hydrogen sulphide into a 40 per cent. aqueous solution of formaldehyde acidified with hydrochloric acid, the author has obtained one compound apparently tolerably pure. Crystallised from ether, it melts at 97—103°, volatilises seemingly unchanged, and gives numbers corresponding approximately with the formula $C_4H_8S_3O$ or $C_3H_6S_3 + CH_2O$. It is not, however, a simple additive-

product of trithioformaldehyde and formaldehyde, as it decolorises iodine solution and does not yield a sulphone on oxidation. With lead and copper salts, it gives precipitates, which when warmed with alkalis easily decompose into metallic sulphides. Its general behaviour is thus that of a mercaptan, and when heated with concentrated hydrochloric acid or other dehydrating agents, it yields trithioformaldehyde. When a solution of formaldehyde is saturated with hydrogen sulphide, it remains clear, but on the addition of concentrated hydrochloric acid the solution solidifies suddenly to a crystalline magma consisting mainly of the compound just described. If excess of hydrochloric acid is added, and the whole warmed, the crystalline mass is converted into trithioformaldehyde. Trithioformaldehyde is odourless when pure.

With acetaldehyde similar but liquid products are formed, which have been investigated by Weidenbusch, Klinger, and others. These products yield a more stable, yellow lead-derivative, decolorise iodine solutions, dissolve in caustic soda, and generally have the character of mercaptans. Marckwald has also shown (Abstr., 1886, 864) that thioacetaldehyde unites with water to form hydroxyethylmercaptan, $SH{\cdot}CHMe{\cdot}OH$, which under water gradually changes to the oily products just described. L. T. T.

Thioaldehydes. By E. BAUMANN and R. CAMPS (*Ber.*, **23**, 69—73).—Baumann and Fromm showed (this vol., p. 25) that α- and β-trithioaldehydes were both oxidised by potassium permanganate in acid solutions to a stable trisulphone, $C_6H_{12}S_3O_6$. The authors have now investigated the oxidation of trithioformaldehyde. The oxidation is best effected by making a paste of the aldehyde with dilute sulphuric acid and adding gradually thereto a concentrated solution of potassium permanganate. *Trimethylenetrisulphone*, $CH_2<\begin{matrix}SO_2{\cdot}CH_2\\SO_2{\cdot}CH_2\end{matrix}>SO_2$, forms a crystalline powder insoluble in water, alcohol, ether, chloroform, glacial acetic acid, or dilute acids. It dissolves in caustic soda, warm aqueous ammonia, and also in boiling sodium carbonate solution, from which it expels carbonic anhydride. Neither concentrated nitric nor sulphuric acid acts on it in the cold or when gently warmed with it, but the latter dissolves it when strongly heated, the unchanged substance crystallising out again on cooling. Only at its boiling point does sulphuric acid cause partial decomposition. When the trisulphone is heated alone, a part sublimes, the remainder charring without previous fusion. The trisulphone has the character of a hexabasic acid, all six atoms of hydrogen being replaceable by basic radicles. When it is dissolved in a large excess of soda and the solution treated with excess of methyl iodide, triacetonetrisulphone, $C_9H_{18}S_3O_6$ (this vol, p. 26), is formed. With less alkali and methyl iodide, less highly methylated compounds are formed.

Compounds less highly oxidised than the trisulphone were also present in small quantities among the oxidation-products, and were less soluble in soda. One of these appeared to be a disulphone, but was not obtained in a pure state. L. T. T.

Anhydride Formation in Acids of the Succinic Series. By K. AUWERS and V. MEYER (*Ber.*, **23**, 101—103).—The readiness with which anhydride formation takes place in acids of the succinic series is increased by the presence of methyl-groups in the molecule.

Tetramethylsuccinic acid, for example, is converted into the anhydride on distilling, when heated with hydrochloric acid under pressure, or when distilled with steam; in the last case the change is not complete.

Trimethylglutaric acid gives an anhydride far more readily than glutaric acid, but not so easily as tetramethylsuccinic acid; it is not acted on by boiling water, but on distillation it yields the anhydride.

When trimethylglutaric acid is brominated according to Hell's method, it yields bromotrimethylglutaric anhydride.

Trimethylsuccinic acid has been prepared. F. S. K.

Tetramethylsuccinic Acid and Trimethylglutaric Acid. By K. AUWERS and V. MEYER (*Ber.*, **23**, 293—311; compare Abstr., 1889, 1145, and Zelinsky, this vol., p. 132).—The two acids, melting at 97° and 190° respectively, which are obtained by treating ethyl α-bromisobutyrate with finely divided silver and hydrolysing the fraction of the product boiling at 200—250° with concentrated hydrobromic acid at 100°, have been proved to be trimethylglutaric acid and tetramethylsuccinic acid respectively. The two compounds can be easily separated by distillation with steam. The tetramethylsuccinic acid passes over for the most part in the form of the anhydride, and is best isolated by evaporating the distillate to a small volume with alkali, then acidifying, and separating the precipitated acid by filtration. The non-volatile trimethylglutaric acid is extracted with ether, the ether evaporated, and the residue recrystallised from hot water. The yield of the two products together is about 15 per cent. of the theoretical quantity, and they are obtained in about equal quantities.

Tetramethylsuccinic acid, $C_8H_{14}O_4$, melts at 190—192° when heated slowly, but when heated quickly the temperature may rise to about 200° before it becomes liquid; it forms short, dendritic crystals, is readily soluble in alcohol and benzene, and moderately easily in ether, chloroform, carbon bisulphide, and hot water, but only sparingly in cold water, and is almost insoluble in light petroleum. Molecular weight determinations by Beckmann's method in ethereal solution, and by Raoult's method in glacial acetic acid solution, gave results in accordance with the molecular formula given above. An examination of the electrical conductivities of tetramethylsuccinic acid and trimethylglutaric acid proved that the higher melting compound only is a substituted succinic acid, and measurements of the electrical conductivities of the sodium salts of the two acids gave results which showed that both compounds are dicarboxylic acids.

Tetramethylsuccinic anhydride, $C_8H_{12}O_3$, is best prepared by distilling the acid or heating it for a short time at its boiling point. It crystallises from hot light petroleum in small, colourless needles, melts at 147°, and boils at 230·5°. It is very readily soluble in most ordinary solvents, but only sparingly in cold light petroleum, and almost in-

soluble in cold water or sodium carbonate. It is quickly decomposed by hot alkalis, and on acidifying, the acid is precipitated.

When tetramethylsuccinic acid is treated with bromine and amorphous phosphorus by Hell-Volhard's method, and the product dropped on to ice, the anhydride is obtained, but not a trace of any brominated acid is formed.

Trimethylglutaric acid, $COOH{\cdot}CMe_2{\cdot}CH_2{\cdot}CHMe{\cdot}COOH$, crystallises from hot water in plates, melts at 97°, and is very readily soluble in most ordinary solvents, but less readily in carbon bisulphide and light petroleum. Molecular weight determinations by Beckmann's method in ethereal solution, and by Raoult's method in glacial acetic acid solution, gave results in accordance with the molecular formula $C_8H_{14}O_4$.

The *anhydride*, $C_8H_{12}O_3$, can be prepared by boiling the acid for a long time, or by treating it with acetic chloride. It crystallises from hot light petroleum in compact, colourless needles, melts at 95—96°, and boils at 262°. It is much more readily decomposed by water and sodium carbonate, but in other respects it resembles the anhydride of tetramethylsuccinic acid.

α-Bromotrimethylglutaric anhydride, $CH_2{<}\begin{matrix}CMe_2-CO\\CBrMe{\cdot}CO\end{matrix}{>}O$, is obtained as follows:—The acid is mixed with a little amorphous phosphorus, and bromine gradually added to the mixture; the product is kept for 24 hours, then heated for a short time on the water-bath, and, when cold, gradually mixed with ice. The precipitate is washed, dried, and recrystallised from hot light petroleum. It forms colourless needles, melts at 114°, sublimes without decomposition, and is readily soluble in all ordinary organic solvents except light petroleum.

Hydroxytrimethylglutaric acid lactone, $\begin{matrix}CMe_2{\cdot}CH_2\\|\qquad\\CO\text{——}O\end{matrix}{>}CMe{\cdot}COOH$, is obtained when the preceding compound is treated with soda, boiling water, or sodium carbonate; the solution is acidified if necessary, and the product extracted with ether. It separates from ether in transparent, well-defined crystals, melts at 103—104°, and is readily soluble in water, alcohol, ether, benzene, and chloroform, but less readily in carbon bisulphide, and only sparingly in light petroleum. It sublimes without decomposition, but it is not volatile with steam. The *silver* salt, $C_8H_{11}O_4Ag$, is a colourless, crystalline compound.

F. S. K.

Tricarballylates. By E. GUINOCHET (*Compt. rend.*, **110**, 47—49). —The tricarballylates closely resemble the aconitates, but the tribasic salts of tricarballylic acid are neutral to litmus and phenolphthaleïn, whilst those of aconitic acid are alkaline.

The *monopotassium* salt crystallises with 2 mols. H_2O in colourless, transparent films which become anhydrous in a dry vacuum. The *sesquipotassium* salt, $C_6H_7KO_6,C_6H_6K_2O_6 + \frac{1}{2}H_2O$, is a crystalline powder which loses water at 100° and decomposes at 130°; the *tripotassium* salt forms very deliquescent nodules containing 1 mol. H_2O, which is given off at 215°, the salt decomposing at 240°. The *monosodium* salt crystallises with 1 mol. H_2O in transparent prisms which

become anhydrous at 100°; the *disodium* salt forms crystalline crusts which contain 1 mol. H_2O, become anhydrous at 110°, and decompose at 135°; the *trisodium* salt forms very soluble, prismatic needles which contain ½ mol. H_2O, and when dried do not decompose below 160°. The *sesquiammonium* salt forms anhydrous, striated, nacreous, hexagonal plates; the *triammonium* salt crystallises with 1 mol. H_2O in very deliquescent, slender needles. The *trilithium* salt crystallises with 2 mols. H_2O in very soluble, prismatic needles which lose one-half their water at 130°, become anhydrous at 185°, and do not alter at 250°. The *monocalcium* salt forms slender needles which contain 1 mol. H_2O and decompose at 125°; the *tricalcium* salt forms a white, amorphous powder which contains 3 mols. H_2O, one-third being given off at 100°, and the remainder at 150°, whilst the salt decomposes at 200°. If this latter salt is made by neutralising tricarballylic acid with lime-water, a precipitate only forms in concentrated solutions; if concentrated solutions of tripotassium tricarballylate and calcium chloride are mixed, no precipitate forms until the liquid is boiled. The *tribarium* salt, after being dried in a vacuum, contains 7 mols. H_2O, one of which is expelled at 100°, and the remainder at 200°; but the salt does not decompose even at 250°. The *trimagnesium* salt crystallises with 3 mols. H_2O, loses one at 100°, and the remainder at 165°, and decomposes at 200°.

The *aluminium* salt, obtained by double decomposition, is a gelatinous precipitate which when dry forms a bulky, white, very hygroscopic powder; it is a hydrated, basic salt, and has the composition $(C_6H_5O_6)_2Al_2 + Al_2O(OH)_4$, becomes anhydrous at 150°, and decomposes at 200°. The *chromium* salt is prepared in a similar manner, has a similar composition, and forms a very hygroscopic, grey-blue powder. The *nickel* salt crystallises with 5 mols. H_2O, loses one at 100°, three at 200°, the last at 225°, and decomposes at 240°; its solution becomes turbid at 60°, and at 100° deposits an abundant precipitate of a lower hydrate containing 3 mols. H_2O; this becomes anhydrous at 150° and decomposes at 200°. The *cobalt* salt is a wine-red, hygroscopic powder, which when dried at the ordinary temperature contains $4H_2O$, but decomposes above 200°; if the solution is heated, it deposits a precipitate, which after drying at 100° is violet-blue, contains 1 mol. H_2O, and decomposes at 110°. The *zinc* salt forms prismatic crystals, and if its solution is heated, a crystalline powder is deposited which contains $\frac{1}{2}H_2O$ and becomes anhydrous at 100°; the addition of alcohol to the cold aqueous solution precipitates a monohydrated salt which becomes anhydrous at 190°, and decomposes at 220°. The *cupric* salt is obtained by double decomposition as a blue, flocculent precipitate which when dry contains 2 mols. H_2O and decomposes above 140°. The *lead* salt is a dense, white, insoluble powder, and the *silver* salt is dense and white, and alters but little when exposed to light. C. H. B.

Action of Oxygen on Zinc Ethyl. By R. DEMUTH and F. MEYER (*Ber.*, **23**, 394—398).—In the course of his classical researches on zinc ethyl, Frankland studied the action of oxygen on this substance, and obtained a white compound which he regarded as a mixture

of zinc oxide, ethoxide, and acetate (*Annalen*, **95**, 46). This result appeared to the authors very remarkable, as in processes of oxidation the oxygen is not as a rule interposed between two atoms which are directly connected. (The formation of acids from aldehydes is only an apparent exception, as this reaction probably always takes place in presence of water.) They have therefore re-examined the subject, and find that when oxygen or air is passed through zinc ethyl diluted with light petroleum, a beautiful white powder is obtained which contains no acetic acid. Its composition is not constant, but varies in the different preparations. As previously stated by Frankland, it decomposes on heating with violent evolution of gas, scattering white flocks around, and sometimes exploding violently. These properties can hardly belong to a substance having the constitution $Zn(OC_2H_5)_2$, and the authors regard it as a peroxide of the formula ZnEt·O·OEt. In favour of this view is the fact that it causes separation of iodine from an acid solution of potassium iodide even in absence of air, and yields ethyl alcohol on distillation with dilute sulphuric acid, but no ethane. The latter result shows that it cannot have the constitution ZnEt·OEt.

Zinc ethoxide is also stated by Butlerow and Lissensko (*Jahresb.*, 1864, 467, 470) to be formed by the action of zinc ethyl on absolute alcohol. A white powder is indeed thus obtained, which decomposes quietly on heating, but yields no alcohol on distillation with dilute sulphuric acid, and cannot, therefore, be zinc ethoxide. This compound has, therefore, not yet been prepared. H. G. C.

Chloropyromucic Acids. By H. B. Hill and L. L. Jackson (*Amer. Chem. J.*, 12, 22—51).—Ethyl pyromucate was made by warming a solution of 3 parts of pyromucic acid in 5 parts of absolute alcohol with 3 parts of concentrated sulphuric acid (sp. gr. 1·84) for four hours on a water-bath, allowing the mixture to cool, and treating it with water. The crude ether thus obtained was washed with sodium carbonate, dried by exposure to air, and purified by distillation; the yield was 68 per cent. of the theoretical. The distillate was treated with chlorine at 0° until it ceased to gain in weight, and then fractionally distilled at a pressure of 15 mm. Some ethyl chloropyromucate [COOH : Cl = 2 : 5] was formed, but the main product was ethyl pyromucate tetrachloride, $C_4H_3Cl_4O·COOEt$, which formed the fraction distilling between 150° and 160°.

Chloropyromucic acid [COOH : Cl = 2 : 5] was obtained in the following manner:—Ethyl pyromucate was heated at 145°, and chlorine passed through it until the gain in weight corresponded with the substitution of an atom of chlorine for one atom of hydrogen. The viscous liquid was added to a concentrated alcoholic solution of soda, and the sodium salt of chloropyromucic acid thus obtained was decomposed with dilute acid, and the crude acid formed crystallised from benzene; the yield was 38 per cent. of the theoretical. It melts at 176—177°, dissolves readily in alcohol and ether, and also in benzene or water when hot but not when cold; 100 parts of water dissolve 0·28 part of it at 19·5°. The *barium* (with 1 mol. H_2O) and *calcium* (with $3H_2O$) *salts* were prepared; 100 parts of water at 19·5°

dissolve 5·67 and 1·12 parts respectively of these salts. The *potassium* and *silver salts* were also prepared; the latter is only slightly soluble in water.

Ethyl chloropyromucate (2 : 5) was prepared by treating the acid with alcohol and sulphuric acid; it is a heavy, colourless oil, melting at 1—2°, and boiling at 216—218° at a pressure of 77 mm. By treating it with ammonia, *chloropyromucamide* (2 : 5) was obtained; it can, however, be better prepared from the acid chloride and solid ammonium carbonate. It crystallises from water in slender needles melting at 154—155°. This chloropyromucic acid, when treated with bromine and water, yields fumaric acid, the reaction taking place according to the equation $C_5H_3ClO_3 + 2Br_2 + 3H_2O = C_4H_4O_4 + CO_2 + 4HBr + HCl$. When oxidised with nitric acid, it also yields fumaric acid. This shows that it must have the formula [COOH : Cl = 2 : 5].

Chloropyromucic acid [COOH : Cl = 2 : 3] was made from dichloropyromucic acid [COOH : $(Cl)_2$ = 2 : 3 : 5] by dissolving it in 20 parts of dilute ammonia, adding an equal weight of zinc-dust, and boiling the solution for 10 hours, taking care to keep it strongly alkaline. The solution was filtered, cooled, and treated with dilute sulphuric acid, the crude acid which separated was dissolved in dilute ammonia, and calcium chloride added to the solution as long as a sparingly soluble calcium salt was precipitated. The acid was then obtained by filtering the solution and acidifying it with hydrochloric acid; it was recrystallised from water; the yield was 80 per cent. of the theoretical. It was also obtained, though less easily, by reducing dichloropyromucic acid (2 : 3 : 4) with sodium amalgam. It melts at 145—146°, and dissolves in alcohol, ether, and in hot benzene, chloroform, and water; 100 parts of water dissolve 0·8 part of it at 19·8°. The *barium* (with 1 mol. H_2O) and *calcium* (with $3H_2O$) *salts* were prepared; of these 100 parts of water dissolve 2 and 3·1 parts respectively at about 19·5°. *Ethyl chloropyromucate* [2 : 3] forms crystals melting at 29—30° and boiling at 217°. This chloropyromucic acid, when treated with bromine and water, gives a *mucochlorobromic acid* melting at 121—122°, according to the equation $C_5H_3ClO_3 + 3Br_2 + 2H_2O = C_4H_2BrClO_3 + CO_2 + 5HBr$. Nitric acid oxidises it in part to chlorofumaric acid.

Dichloropyromucic acid [COOH : $(Cl)_2$ = 2 : 3 : 4] was prepared by passing chlorine over ethyl pyromucate at 0° until it ceased to gain in weight, expelling the excess of chlorine by a current of air, and decomposing the product with excess of alcoholic soda. The sodium salt thus obtained was decomposed with hydrochloric acid, and the dichloropyromucic acid formed was recrystallised from benzene; the yield was 39 per cent. of the theoretical. It melts at 168—169°, and dissolves in alcohol and ether, and in water, benzene, and chloroform when hot; 100 parts of water at 19·5° dissolve 0·27 part of the acid. The *barium* (with $3H_2O$), *calcium* (with $4H_2O$), *potassium*, and *silver salts* were prepared; of the first two, 100 parts of water at 19·5° dissolved 0·46 and 1·21 parts respectively. *Ethyl dichloropyromucate* [2 : 3 : 4] was prepared by acting on the acid with alcohol and sulphuric acid; it crystallises from alcohol in large needles melting at 63—64°. When treated with strong aqueous ammonia, it forms *dichloropyromucamide*

[2 : 3 : 4], melting at 176—177°. This dichloropyromucic acid yields mucochloric acid melting at 124—125°, when treated with bromine and water, according to the equation $C_5H_2Cl_2O_3 + 2Br_2 + 2H_2O = C_4H_2Cl_2O_3 + CO_2 + 4HBr$. When oxidised with nitric acid, it yields both mucochloric and dichlormaleic acids, and must therefore have the formula [$COOH : Cl_2 = 2 : 3 : 4$].

Dichloropyromucic acid [$COOH : Cl_2 = 2 : 3 : 5$] was obtained by distilling ethyl pyromucate tetrachloride at 16 mm. pressure, and formed the greater part of the fraction boiling between 110° and 113°. Another dichloropyromucic acid of unknown formula, and chloropyromucic acid [2 : 5] were also formed; the separation of these acids was a tedious matter, and reference must be made to the original paper for details. Dichloropyromucic acid [2 : 3 : 5] melts at 155—156°, and sublimes unaltered at a higher temperature. It dissolves in ether, in alcohol, and in hot water, benzene, or chloroform; 100 parts of water at 19·5 dissolve 0·26 part of the acid. The *barium* (with $4H_2O$) and *calcium* (with $3H_2O$) *salts* were prepared; 100 parts of water at 19·5° dissolve 0·42 and 0·22 part respectively of these salts. *Ethyl dichloropyromucate* [2 : 3 : 5] was prepared by the action of ethyl iodide on the silver salt of the acid; it is a heavy liquid, melts at 2—3°, and boils at 116—118° at 16 mm. pressure. When treated with concentrated aqueous ammonia at 100°, it yields *dichloropyromucamide* [2 : 3 : 5] melting at 153—154°. The acid itself is but slowly attacked by nitric acid, but when treated with bromine and water, it yields chlorofumaric acid according to the equation $C_5H_2Cl_2O_3 + 2Br_2 + 3H_2O = C_4H_3ClO_4 + CO_2 + HCl + 4HBr$; hence it must have the constitution [$COOH : Cl_2 = 2 : 3 : 5$].

C. F. B.

Dependence of Substitution Phenomena on the Atomic or Molecular Weights of certain Atoms or Groups. By F. KEHRMANN (*Ber.*, **23**, 130—136; compare *J. pr. Chem.* [2], **40**, 257).—The study of substitution phenomena, especially in the aromatic series, shows that the so-called orientation rules are dependent on the atomic or molecular weight of the atom or radicle which dominates or directs the position taken up by the substituting-group, as well as on the law of affinity. Monhydroxy- and monamido-derivatives of benzene, for example, give both ortho- and para-substitution products, but when the molecular weight of the hydroxy- or amido-group is increased by an alkyl or an acid radicle, the para-substitution compound is the principal, or the sole product.

The lack of data makes it impossible as yet to formulate any general law, but in a few cases the observed facts are sufficient to show the influence of atomic or molecular weight. In the substitution of the homologues of benzene with two different alkyls, the entering group takes up with preference the ortho-position to that radicle which has the lower molecular weight. Parethyltoluene, for example, yields a brominated derivative [$Me : Br : Et = 1 : 2 : 4$]; paracymene gives a sulphonic acid [$Me : SO_3H : Br = 1 : 2 : 4$], and only small quantities of the isomeride.

In the substitution of dihalogen benzene-derivatives with two different halogens, the greater negative influence of the halogen of

lower atomic weight is overcome by the influence due to the atomic weight *per se*. Metachlorobromobenzene, for example, probably gives a mixture of two nitro-compounds, but the substance [$Cl : NO_2 : Br = 1 : 2 : 5$] is formed in larger quantity; parachloriodobenzene gives most probably, the compound [$Cl : NO_2 : I = 1 : 2 : 4$].

F. S. K.

Nitro-derivatives of Metabromotoluene. By W. B. Bentley and W. H. Warren (*Amer. Chem. J.*, **12**, 1—7).—Metabromodinitrotoluene, melting at 103—104°, has been prepared by Grete (*Annalen*, **168**, 258) by acting on metabromotoluene or metabromomononitrotoluene with fuming nitric acid, and more recently by Jackson and Robinson (this vol., p. 377) by the decomposition of ethyl bromodinitrophenylmalonate.

The authors have determined its constitution to be

$$[Me : Br : (NO_2)_2 = 1 : 3 : 4 : 6]$$

from the following reasons:—(1) Grete obtained it from a mononitrometabromotoluene, which he showed must have the NO_2-group in the *ortho*-position, because when reduced it gave a bromotoluidine identical with that obtained by acting on *ortho*acetotoluide with bromine; (2) Nevile and Winther (Trans., 1880, 429) showed that when in the metabromotoluidine mentioned above, the NH_2-group is displaced by bromine, a dibromotoluene is obtained identical with that obtained by v. Richter (this Journal, 1875, 73) from *para*dibromobenzene; the nitrobromotoluene from which it is derived must therefore have the formula [$Me : Br : NO_2 = 1 : 3 : 6$]; (3) the authors heated this nitrobromotoluene with alcoholic ammonia, and converted it into a dinitrometatoluidine melting at 193—194°. The latter substance was then dissolved in a mixture of acetone and alcohol and treated with sulphuric acid and sodium nitrite; dinitrotoluene [$Me : (NO_2)_2 = 1 : 4 : 6$], melting at 71°, was thus obtained. This shows that the two NO_2-groups occupy respectively the *ortho*- and *para*-positions with regard to the methyl, and hence that the metabromodinitrobenzene under consideration must have the formula [$Me : Br : (NO_2)_2 = 1 : 3 : 4 : 6$]. The dinitrotoluidine mentioned above had been previously prepared by Hepp by acting on γ-trinitrotoluene with alcoholic ammonia, and by Kolb from dinitrocresol ether. Hepp's γ-trinitrotoluene must therefore have the formula [$Me : (NO_2)_3 = 1 : 3 : 4 : 6$].

Metabromotrinitrotoluene [$Me : Br : (NO_2)_3 = 1 : 3 : 2 : 4 : 6$] was prepared by treating metabromodinitrotoluene with a mixture of fuming nitric acid and sulphuric acid; the yield was about 60 per cent. of the theoretical. It crystallises from alcohol in small, white needles melting at 143°. It is insoluble in water or light petroleum, nearly insoluble in cold alcohol, sparingly soluble in carbon bisulphide, soluble in ether, methyl alcohol, benzene, chloroform, glacial acetic acid, and acetone. It is not acted on by aqueous soda, or by strong acids, but the bromine is easily removed by the action of alcoholic ammonia or aniline. When treated with alcoholic ammonia, it gives a trinitrotoluidine melting at 136°, identical with that obtained from trinitrometacresol ether by Nölting and Salis (Abstr.,

1885, 59), who assigned to it the formula [$Me : NH_2 : (NO_2)_3 = 1 : 3 : 2 : 4 : 6$]. Hence metabromotrinitrotoluene must have the formula given above.

Anilidotrinitrotoluene [$Me : NHPh : (NO_2)_3 = 1 : 3 : 2 : 4 : 6$] was prepared by treating metabromotrinitrotoluene with aniline. It crystallises from a mixture of alcohol and benzene in well-developed, shining, yellow plates melting at 151°. It is insoluble in water or light petroleum, sparingly soluble in ethyl or methyl alcohol, soluble in ether, chloroform, benzene, carbon bisulphide, glacial acetic acid, and acetone. It dissolves in aqueous soda, giving a red solution from which hydrochloric acid precipitates the original substance unaltered. It dissolves in strong sulphuric or strong nitric acid, but not in strong hydrochloric acid. C. F. B.

Derivatives of Paranitrobenzyl Chloride. By A. HAFNER (*Ber.*, **23**, 337—345).—In agreement with Salkowski's results (Abstr., 1889, 1174), the author finds that paranitrobenzyl chloride may be readily converted into paranitrobenzylamine, $NO_2\cdot C_6H_4\cdot CH_2\cdot NH_2$, by Gabriel's method (Abstr., 1887, 1037). It forms a strongly basic oil which absorbs carbonic anhydride from the air, solidifying to white crystals. Its *hydrochloride* crystallises in colourless needles which are soluble in water, and commence to decompose at 220°, whilst the *nitrate* forms citron-yellow, flat needles which decompose at 200°. The *platinochloride* and *picrate* have also been prepared.

Paranitrobenzyl alcohol, $NO_2\cdot C_6H_4\cdot CH_2\cdot OH$, is prepared by warming a dilute solution of the hydrochloride with sodium nitrite. It separates in slender, colourless needles which melt at 93°. This compound has been previously prepared by Beilstein and Kuhlberg (*Annalen*, **147**, 343), and by Basler (Abstr., 1884, 310).

Paranitrobenzylacetamide, $NO_2\cdot C_6H_4\cdot CH_2\cdot NHAc$, is obtained by heating the hydrochloride with acetic anhydride and sodium acetate. It forms colourless needles, soluble in water, and melting at 133°. Amsel and Hofmann (Abstr., 1886, 698) found the melting point to be 125°.

The corresponding *paranitrobenzoylbenzamide*, $NO_2\cdot C_6H_4\cdot CH_2\cdot NHBz$, formed by the action of benzoic chloride on paranitrobenzylamine hydrochloride, crystallises from alcohol in fascicular groups of needles which melt at 155—156°.

Paranitrobenzylcarbamide, $NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot CO\cdot NH_2$.—In order to prepare this compound, paranitrobenzylamine hydrochloride is treated with freshly prepared silver cyanate at 100°, the mixture evaporated to dryness, and extracted with alcohol. It separates from the solution in pale-yellow, lance-shaped needles melting at 196—197°. If potassium cyanate be substituted for silver cyanate, no reaction takes place.

By the action of carbon bisulphide on an ethereal solution of paranitrobenzylamine, it is converted into the *dithiocarbamate*,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot CSSH,NH_2\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

a yellow, crystalline mass which darkens at 120°, melts at 193°, and is converted on boiling with excess of alcohol into hydrogen sulphide

and *paradinitrobenzylthiocarbamide*, $CS(NH{\cdot}C_7H_6{\cdot}NO_2)_2$. This crystallises in brown, nodular groups of needles which melt with decomposition at 202°, are sparingly soluble in alcohol, and somewhat more readily in acetic acid. Mercuric oxide converts it into the corresponding *paradinitrobenzylcarbamide*, which is also formed by mixing an ethereal solution of paranitrobenzylamine with a solution of carboxyl chloride in benzene. It crystallises from acetic acid in silvery needles which begin to decompose at 224°, and melt completely at 234°. They dissolve in alcohol with difficultly, and are insoluble in ether.

Ethyl paranitrobenzylcarbamate, $NO_2{\cdot}C_7H_6{\cdot}NH{\cdot}COOEt$, is readily produced by mixing an ethereal solution of the amine with ethyl chlorocarbonate. It crystallises from ether in concentrically grouped needles melting at 116—117°.

When paranitrobenzylphthalimide is reduced by tin and hydrochloric acid, it is converted into a base, $C_{15}H_{14}N_2O$, which has the constitution $C_6H_4{<}\substack{CO-\\CH_2}{>}N{\cdot}C_7H_6{\cdot}NH_2$ or $CH_2{<}\substack{C_6H_4\\-O-}{>}C{:}N{\cdot}C_7H_6{\cdot}NH_2$, and is therefore *paramidobenzylphthalimidine*. It forms colourless plates which have a mother-of-pearl lustre, and melt at 187—188°. A white, crystalline *hydrochloride* was obtained which had the composition $C_{15}H_{14}N_2O,HCl$; but this compound could not be prepared again, a salt being obtained containing a larger quantity of chlorine. The *hydrobromide* has the formula $(C_{15}H_{14}N_2O)_2,3HBr$, is readily soluble in water, and melts with decomposition at 215°. The *platinochloride*, *picrate*, and *stannochloride* have also been prepared and analysed.

Acetylparamidobenzylphthalimidine, $C_8H_6O{:}N{\cdot}C_7H_6{\cdot}NHAc$, is obtained by boiling the base with acetic anhydride. It forms a brown, crystalline powder which is readily soluble in acetic acid, less so in alcohol, and melts at 226—227°.

Parahydroxybenzylphthalimidine, $C_8H_6O{\cdot}N{\cdot}C_7H_6{\cdot}OH$, is prepared by the careful addition of dilute solution of sodium nitrite to a solution of paramidobenzylphthalimidine in hydrochloric acid, and gentle warming. It crystallises from water in long, red, sparingly soluble needles, melts at 187—198° (?), and is readily soluble in alcohol, acetic acid, and fixed alkalis, but insoluble in ammonia.

This compound is split up by hydrochloric acid, with formation of a new base and resinous matter. The former appears to have the composition $C_8H_9NO_2$, and forms a platinochloride which crystallises well.

H. G. C.

Orthonitrobenzyl Sulphide. By R. JAHODA (*Monatsh.*, **10**, 874—883).—Lellmann and Stickel have shown (Abstr., 1886, 793) that orthobenzylenimide is formed on reduction of orthonitrobenzylic chloride with tin and hydrochloric acid. The author has extended their investigation, using an ammoniacal alcoholic solution of the chloride, and hydrogen sulphide as a reducing agent, and has isolated the following products:—

Orthonitrobenzyl sulphide, $S(CH_2{\cdot}C_6H_4{\cdot}NO_2)_2$, is insoluble in water, but dissolves readily in hot alcohol, benzene, chloroform, and acetic

acid, and crystallises from these solvents in monoclinic, pale-yellow plates, $a : b : c = 0.53623 : 1 : 1.04866$; it melts at 124°. On reduction with tin and hydrochloric acid, the corresponding amido-benzyl sulphide is formed, which is readily soluble in alcohol and ether, melts at 70°, and gives a hydrochloride very soluble in water and alcohol; this decomposes at 200° without previously melting. Orthonitrobenzyl sulphide is slowly attacked when heated in a water-bath with nitric acid of sp. gr. 1·3; but may be more readily oxidised by heating at 100° in sealed tubes with concentrated nitric acid, or by treating a solution in acetic acid with potassium permanganate, the sulphoxide, $SO(CH_2{\cdot}C_6H_4{\cdot}NO_2)_2$, being formed. It is readily soluble in alcohol and ether, and on oxidation with a large excess of fuming nitric acid or with permanganate is converted into the sulphone, $SO_2(CH_2{\cdot}C_6H_4{\cdot}NO_2)_2$, which crystallises in slender, white, silky needles melting at 200°.

Orthonitrobenzyl bisulphide, $S_2(CH_2{\cdot}C_6H_4{\cdot}NO_2)_2$, is readily soluble in warm alcohol, from which it separates on cooling as a seemingly amorphous mass melting at 47°. It may be obtained in the crystalline form by allowing the alcoholic solution to evaporate very slowly, is volatile in a current of steam, and has a very irritating odour. On reduction with tin and hydrochloric acid, it gives a hydrosulphide which produces a red colour with ferric chloride. On treatment with mercuric chloride, the bisulphide forms a heavy white precipitate. G. T. M.

Compounds of Volatile Fatty Acids with Phenols. By M. v. Nencki (*Monatsh.*, 10, 906—907; compare Perkin, Trans., 1889, 546—549).—The author directs attention to the fact that several compounds of volatile fatty acids with phenols have been previously described by him (Abstr., 1881, 591, 811; 1882, 1201); he now finds that propionic, butyric, and valeric acids, when heated with phenols and zinc chloride, form the corresponding hydroxy-ketones, which mostly crystallise well, are insoluble, or nearly insoluble in water, and dissolve readily in alcohol.

Phenyl propionate is readily obtained by heating together propionic acid (1 part), phenol (1 part), and zinc chloride (2 parts), for from 5 to 10 minutes. It dissolves in 30 parts of hot, and 2,900 parts of cold water; gives phenol and parahydroxybenzoic acid on fusion with potash, and consequently has the propionyl-group in the para-position (compare Perkin, *loc. cit.*). Phenyl propionate gives with bromine a crystalline dibromo-derivative, and with nitric acid a characteristic nitro-compound. G. T. M.

Action of Chlorine on Phloroglucinol. By T. Zincke and O. Kegel (*Ber.*, 23, 230—248).—It has been shown in a previous paper (Abstr., 1889, 967) that the final product of the action of dry chlorine on phloroglucinol is hexachlorotriketohexamethylene, $\begin{matrix} CCl_2{\cdot}CO{\cdot}CCl_2 \\ | \qquad\quad | \\ CO{\cdot}CCl_2{\cdot}CO \end{matrix}$, and that this is decomposed by water with formation of carbonic anhydride, tetrachloracetone, and dichloracetic acid. It

seemed probable that two intermediate products must be formed, having the formulæ $CHCl_2·CO·CCl_2·CO·CCl_2·COOH$ and

$$CHCl_2·CO·CCl_2·CO·CHCl_2.$$

No evidence of the formation of these compounds could be obtained, and the further investigation of the action of water has yielded only negative results. If, however, the compound be treated simultaneously with either chlorine or bromine and water, persubstitution-products of acetylacetone are obtained. The action of ammonia and methyl and ethyl alcohols on the compound has also been investigated.

When hexachlorotriketohexamethylene is dissolved in acetic acid, treated with excess of bromine, and 50—60 times the quantity of ice-cold water gradually added, carbonic anhydride is immediately evolved, and a granular-crystalline mass of *hexachlorodibromacetylacetone*, $CBrCl_2·CO·CCl_2·CO·CBrCl_2$, separates. This crystallises from light petroleum in thick, colourless needles or in well-developed prisms which melt at 57—58°; it boils under 25—26 mm. pressure at 200—201°, and is soluble in most of the ordinary solvents with the exception of water. This liquid has no action on the substance in the cold, but, on warming, decomposes it into *tetrachlorobromacetone*, dichlorobromomethane, and carbonic anhydride. The first-named compound is a colourless, refractive oil which has a penetrating odour, boils at 112—114° (30 mm.), and forms a solid hydrate with water. Ammonia converts hexachlorodibromacetylacetone into *dichlorobromacetamide*, $CCl_2Br·CO·NH_2$, which forms large, quadratic tables or thick needles melting at 139°. Aniline gives a mixture of compounds amongst which is dichloracetanilide; whilst with alkali, a mixture of the potassium salts of dichloracetic and dichlorobromacetic acids, together with dichlorobromomethane, appears to be the chief product.

Chlorine and water act on an acetic solution of hexachlorotriketohexamethylene in exactly the same manner as bromine and water, *octochloracetylacetone* being formed. This crystallises from light petroleum in thick needles or prisms, melts at 42—43°, and boils at 165—168° (30—32 mm). It is decomposed by hot water into pentachloracetone, and trichloracetic acid or its decomposition-products, whilst ammonia converts it into trichloracetamide; this crystallises from water in thick, colourless needles or tablets melting at 141°, and is identical with the compound prepared from trichloracetic acid.

The action of the halogen and water on hexachlorotriketohexamethylene may be readily explained if the formation of hypochlorous acid is presupposed, in the manner shown by the following equations:—

$$\text{I.}\quad \begin{matrix} CO·CCl_2·CO \\ | \qquad\quad | \\ CCl_2·CO·CCl_2 \end{matrix} + ClOH = CCl_3·CO·CCl_2·CO·CCl_2·COOH.$$

$$\text{II.}\quad CCl_3·CO·CCl_2·CO·CCl_2·COOH + ClOH = \\ CCl_3·CO·CCl_2·CO·CCl_3 + OH·CO·OH.$$

When ammonia gas is passed into a solution of hexachlorotriketohexamethylene in benzene, the reaction takes place very quietly.

dichloracetamide being the sole product. This forms hard, prismatic crystals melting at 98—99°.

The action of aniline is much more complicated: dichloracetanilide is the chief product, but monochloracetanilide, a bromacetanilide, aniline hydrobromide, and probably a brominated aniline, are also formed.

Methyl alcohol acts on hexachlorotriketohexamethylene with formation of tetrachloracetone and methyl dichloromalonate. The reaction is represented by the equation $\begin{matrix} CCl_2\cdot CO\cdot CCl_2 \\ | \qquad\quad | \\ CO\cdot CCl_2\cdot CO \end{matrix} + 2MeOH =$ $CHCl_2\cdot CO\cdot CHCl_2 + COOMe\cdot CCl_2\cdot COOMe$. The latter compound cannot be obtained pure by fractionation, and probably contains a small quantity of a compound analogous to that formed by ethyl alcohol, and described below. With ammonia, however, it yields dichloromalonamide, $CCl_2(CO\cdot NH_2)_2$; this crystallises in rhombic tables, frequently aggregated to broad needles or plates, melts at 203°, and is identical with the compound prepared directly from malonic acid.

Ethyl alcohol acts on hexachlorotriketohexamethylene in a different manner. A smaller quantity of tetrachloracetone is formed, and another compound is obtained boiling at 133—134° under 19—20 mm. pressure, and at 239° with slight decomposition under the ordinary pressure. The constitution of this substance has not yet been proved, but it appears probable that it has the formula

$$CHCl_2\cdot C(OH)(OEt)\cdot CCl_2\cdot COOEt.$$

With caustic potash, it gives dichloracetic acid only, with ammonia dichloracetamide, and with aniline dichloracetanilide, which agrees with the above formula. H. G. C.

Behaviour of Aniline with Substituted Hydroxybenzoic Acids at a High Temperature. By R. SEIFERT (*Ber.*, **23**, 118—120).—Remarks on Limpricht's paper (this vol., p. 158). The compounds obtained by Limpricht and described as new substances have been previously prepared. Limpricht's phenylimidophenol, diacetylphenylimidophenol, and diphenylimidophenylene are the well-known compounds phenylparamidophenol, diacetylphenylparamidophenol, and diphenylparaphenylenediamine respectively. The reaction studied by Limpricht probably takes places in two phases, both of which, when taken singly, are well-known reactions.

F. S. K.

Formation of Triphenodioxazine by the Oxidation of Orthamidophenol. By P. SEIDEL (*Ber.*, **23**, 182—189).—The garnet-red dye obtained by G. Fischer (Abstr., 1879, 924) by the oxidation of orthamidophenol hydrochloride in aqueous solution with potassium ferricyanide, is best prepared by passing a rapid current of air for many days through the hydrochloride dissolved in 30—40 times its weight of water, and heated in a reflux apparatus on a water-bath; a brownish-red, granular precipitate is obtained at first, but this becomes darker in colour and less pure towards the end of the

reaction. The dye can only be purified by careful sublimation, and has the composition $C_{18}H_{10}N_2O_2$, being regarded by the author as *triphenodioxazine*, $C_6H_4<^{N}_{O}>C_6H_2<^{N}_{O}>C_6H_4$, a view which derives confirmation from the fact that it can be prepared synthetically by carefully heating a mixture of anhydrous symmetrical diamidoresorcinol sulphate (1 mol. prop.) with orthamidophenol (2 mol. prop.) to its fusing point. The dye is almost insoluble in water, alcohol, ether, acetone, carbon bisulphide, pyridine, benzene, &c., but gives with all these solvents, except water, solutions which show a beautiful green fluorescence. From xylene (solubility 1 in 1000 at 140°), nitrobenzene (solubility 1 in 100 at 200°), aniline, azobenzene, naphthalene, &c., it crystallises in dark-red forms showing a bluish lustre. When rapidly heated, it can be fused; at 250° it begins to sublime, and at temperatures above 300° is converted into a beautiful, pure green vapour. The dye is not affected by prolonged boiling with concentrated aqueous or alcoholic alkalis, does not form an acetyl-derivative when heated with acetic anhydride, is not oxidised by chlorine or a hot solution of chromic acid in acetic acid, but yields orthamidophenol on reduction with concentrated hydriodic acid at 170°. When warmed with concentrated sulphuric acid, it is converted into a sulphonic acid, which forms sparingly soluble, cantharides-green potassium and sodium salts, whilst with concentrated nitric acid in acetic acid solution it yields a sparingly soluble nitro-derivative crystallising in brown, bronze-lustred crystals. The *hydrochloride*, $C_{18}H_{10}N_2O_2.2HCl$, crystallises in beautiful, dark cantharides-green needles, and decomposes on treatment with water. The *leuco*-base, $C_{18}H_{12}N_2O_2$, is formed when the dye is heated at 120° with a solution of phenylhydrazine in xylene. It crystallises in colourless scales, is sparingly soluble in the ordinary solvents, and when heated either alone at 250—300°, or in solution in nitrobenzene, aniline, or pyridine, is reconverted into the red dye. Its *diacetyl*-derivative, $C_{18}H_{10}N_2O_2Ac_2$, crystallises in colourless scales, melts at 295°, decomposes at higher temperatures with the production of the red dye, and is somewhat more soluble in nitrobenzene, aniline, pyridine, &c., than the leuco-base. W. P. W.

Formation of Alkyl-derivatives of Amides. By J. TAFEL and C. ENOCH (*Ber.*, **23**, 103—108).—*Silver benzamide*, C_7H_6NOAg, prepared by dissolving benzamide (1 mol.) and silver nitrate (1 mol.) in warm water, and gradually adding the calculated quantity of soda, is a colourless, semi-crystalline powder, which is decomposed by warm water. When treated with ethyl iodide in the cold, it yields benzimido ethyl ether, NH:CPh·OEt, identical with the compound obtained by Pinner (Abstr., 1883, 1089) from benzonitrile and alcoholic hydrogen chloride. When silver benzamide is covered with ether, and treated with hydrogen chloride or hydrogen sulphide, it is reconverted into benzamide.

Anisamide melts at 161—162°, and not at 137—138°, as stated by Henry. The *silver*-derivative has the composition $C_8H_8O_2NAg$.

Anisimido ethyl ether, OEt·C(NH)·C_6H_4·OMe, prepared by treating

silver anisamide with ethyl iodide at 40°, crystallises in long, colourless needles, melts above 30°, and boils without decomposition under greatly reduced pressure. It is soluble in alcohol and ether, and is decomposed by boiling water. The *hydrochloride*, $C_{10}H_{13}O_2N,HCl$, melts at 130° with decomposition, and is soluble in water and alcohol, but insoluble in ether. The *oxalate*, $C_{10}H_{13}O_2N,C_2H_2O_4$, crystallises in colourless needles, melts at 136°, and is soluble in water and alcohol, but insoluble in ether. The *platinochloride*, $(C_{10}H_{13}O_2N)_2,H_2PtCl_6$, crystallises in yellow needles, and is only sparingly soluble in hot alcohol, but soluble in, and partially decomposed by water.

Anisamidine hydrochloride, $NH_2{\cdot}C(NH){\cdot}C_6H_4{\cdot}OMe,HCl$, prepared by treating finely divided anisimido ethyl ether hydrochloride with alcoholic ammonia at 30°, separates from alcohol in colourless crystals, begins to decompose at about 220°, and is readily soluble in water and alcohol, but only sparingly in ether. The free *base*, $C_8H_{10}ON_2$, is a crystalline, hygroscopic compound, very readily soluble in alcohol, but insoluble in ether; the aqueous solution has a strongly alkaline reaction. The *platinochloride*, $(C_8H_{10}ON_2)_2,H_2PtCl_6$, crystallises from hot water in yellow needles. F. S. K.

Identity of Hoffmann's Dibenzylphosphine with Tribenzylphosphine Oxide, &c. By E. A. LETTS and R. F. BLAKE (*Proc. Roy. Soc. Edin.*, **16**, 193—200).—During a previous investigation, Letts found reason to believe that the A. W. Hofmann's dibenzylphosphine (this Journal, 1872, 423) was, in reality, an oxide of tribenzylphosphine, $P(C_7H_7)_3O$. He now finds the melting point to be 215—215·5° (corr.) when recrystallised from alcohol. To estimate the phosphorus, a new method has been devised, the usual processes not being trustworthy when applied to phosphines. A combustion is made with pure copper oxide, and afterwards the contents of the combustion-tube dissolved in nitric acid, and the phosphorus precipitated with ammonium molybdate; figures are given which show the great differences in the percentages as obtained by various processes.

The bromide, chloride, iodide, hydriodide, hydrobromide, platinochloride, nitro-compound, and a double salt with zinc iodide, have been prepared both of Hofmann's compound and of tribenzylphosphine oxide, and in all cases the results were identical. Dibenzylphosphinic acid (m. p. 192°) was also produced by the action of fused potash on both compounds. It seemed probable that the production of the oxide in Hofmann's sealed tube reaction was due to the oxidation of tribenzylphosphine; therefore, the authors sought for the tertiary product in the original product. After much trouble, they isolated a liquid which grew hot on exposure to the air with production both of tribenzylphosphine oxide and of dibenzylphosphinic acid, which was precipitated by hydriodic acid, forming solid compounds, and which in contact with sulphur gives rise to a crystalline compound, believed to be tribenzylphosphine sulphide; the liquid also acts energetically on crystallised benzyl iodide, forming tetrabenzylphosphonium iodide, and is probably a mixture of secondary and tertiary phosphines. From this liquid two solids have been obtained, the one,

almost insoluble in ether, having the formula $(C_7H_7)PO_2$, or $(C_7H_7)_3PS$. The second compound was undoubtedly tribenzylphosphine, and crystallises easily from alcohol, and unites with sulphur and oxygen at the ordinary temperature.

The authors, therefore, consider that in Hofmann's sealed tube reaction hydrogen phosphide acts on benzyl chloride as ammonia does on an alkyl iodide:—(1) $C_7H_7Cl + PH_3 = C_7H_7{\cdot}PH_2,HCl$; (2) $2C_7H_7Cl + PH_3 = (C_7H_7)_2PH,HCl + HCl$; (3) $3C_7H_7Cl + PH_3 = (C_7H_7)_3PHCl + 2HCl$; (4) $4C_7H_7Cl + PH_3 = (C_7H_7)_4PCl + 3HCl$.

It is probable that Hofmann's "dibenzylphosphine" is a product of the reaction of potash on tetrabenzylphosphonium chloride or iodide, an action which Lillie has proved possible—

$$(C_7H_7)_4PCl + KHO = (C_7H_7)_3PO + KCl + C_7H_8.$$

All the possible oxidised derivatives have been isolated from the products of Hofmann's reaction, and they are: benzylphosphinous acid, benzylphosphinic acid, dibenzylphosphinic acid, and tribenzylphosphine oxide.

When benzylphosphine acts on benzyl iodide at the ordinary temperature, the secondary, tertiary, and quaternary compounds are formed.
E. W. P.

Action of Hydroxylamine Hydrochloride on Paradihydroxyparaquinones. By F. KEHRMANN and W. TIESLER (*J. pr. Chem.* [2], **41**, 87—91).—*Chlorhydroxyamidohydroxyquinone oxime*,

$$OH{\cdot}C_6HClO(NOH){\cdot}NH{\cdot}OH,$$

is formed when finely-powdered chlorodihydroxyquinone is left in contact with water and hydroxylamine hydrochloride for several days; the quinone particles change into nearly white, horn-shaped crystals, which decompose without melting, and are almost insoluble in the usual solvents, but soluble in alkalis. When reduced with stannous chloride and hydrochloric acid, it is converted into chlorodiamidoresorcinol. Nitric acid of sp. gr. 1·30 converts it into chlorodinitroresorcinol (m. p. 181°).
A. G. B.

Action of Ethylmalonic Chloride on Ethylbenzene in presence of Aluminium Chloride. By A. BÉHAL and V. AUGER (*Compt. rend.*, **110**, 194—197).—The action of ethylmalonic chloride (45 grams) on ethylbenzene (200 grams) in presence of aluminium chloride (100 grams) yields metadiethylbenzene, which on oxidation is converted into isophthalic acid; sp. gr. at 0° = 0·8812, refractive index at 14° = 1·472. At the same time, a diketone, diethyl-benzoyl ethylmethane, $CHEt(CO{\cdot}C_6H_4Et)_2$ is formed. It boils between 270° and 275° in a vacuum, melts at 88—89°, and crystallises readily from alcohol in needles grouped in nodules. When treated with alkalis, it splits up into paraethylbenzoic acid and ethylphenyl propyl ketone, $PrCO{\cdot}C_6H_4Et$, which boils at 150° under a pressure of 20 mm.; sp. gr. at 0° = 0·9800, refractive index at 14° = 1·499.
C. H. B.

Occurrence of Isocinnamic Acid in the Alkaloïds of Cocaïne. By C. LIEBERMANN (*Ber.*, 23, 141—156).—The decomposition-products of the alkaloïds occurring together with cocaïne contain isocinnamic acid, which can be isolated in the following manner:—The crude product obtained by decomposing the alkaloïds (38 kilos.) with hydrochloric acid is filtered from the solid acids, and the filtrate extracted with ether; on evaporating the ether there remains a semi-solid mass (700—800 grams). This residue is filtered to separate the solid acids, which consist principally of cinnamic acid, together with small quantities of α- and β-truxillic acids and benzoic acid, the oily filtrate is kept for some days at 0°, and again filtered from the crystals which are deposited. The filtrate (300—400 grams) is dissolved in cold sodium carbonate, the solution shaken with ether to remove ethereal salts which may be present, and the acids reprecipitated. The acid mixture is then extracted with warm light petroleum, and the solution evaporated. The crude isocinnamic acid (about 120 grams), obtained in this way in a crystalline condition, is further purified and separated from cinnamic acid by repeatedly extracting it with small quantities of light petroleum, in which cinnamic acid is only very sparingly (0·095 in 100), isocinnamic acid, on the other hand, readily (17 in 100) soluble. It is then converted into the calcium salt, and the latter extracted with water, in which calcium cinnamate is only very sparingly (1 in 430), but calcium isocinnamate readily (1 in 8) soluble. These two processes are repeated many times until the calcium salt obtained is completely soluble in a small quantity of cold water. The salt is then decomposed with hydrochloric acid, and the acid, which is precipitated as an oil, extracted with ether, and recrystallised from light petroleum.

Isocinnamic acid, $C_9H_8O_2$, separates from cold light petroleum in transparent crystals melting at 45—47°; if the acid be coarsely powdered and treated with a small quantity of cold light petroleum in such a way that the more compact crystals remain undissolved, the latter melt at 57°, which is the true melting point of the acid. It is very readily soluble in light petroleum, carbon bisulphide, alcohol, and all ordinary solvents, except water, whereas cinnamic acid and atropic acid are only sparingly soluble in light petroleum and carbon bisulphide. Molecular weight determinations by Raoult's method, in glacial acetic acid solution, gave results in accordance with the molecular formula given above; on evaporating the acetic acid solution on the water-bath, the isocinnamic acid was deposited unchanged. It is immediately oxidised by potassium permanganate in cold sodium carbonate solution, with formation of benzaldehyde, but it does not reduce Fehling's solution, and it is not changed by boiling alcoholic potash. Crystalline measurements showed that this acid is not identical either with cinnamic acid or with atropic acid.

The *calcium* salt, $(C_9H_7O_2)_2Ca + 3H_2O$, separates from cold water in crystals which effloresce on exposure to the air; the salt then contains 3 mols. H_2O, which are expelled at 125°. The *barium* salt is not quite so readily soluble in water as the calcium salt. The *silver* salt, $C_9H_7O_2Ag$, is colourless, and undergoes no change on exposure to light. In aqueous solutions of the ammonium salt, cobalt, man-

ganese, and zinc acetate produce no precipitation, but copper acetate gives a green, and mercuric nitrate a colourless precipitate. The *methyl* salt is a colourless liquid.

Isocinnamic acid begins to boil at 265°, but the boiling point gradually rises to 300°. The distillate consists principally of cinnamic acid (90 per cent.), but on prolonged boiling cinnamene is also produced. Isocinnamic acid is almost quantitatively converted into cinnamic acid when it is boiled for about a minute under the ordinary pressure.

Hydrocinnamic acid (m. p. 48°) is obtained when isocinnamic acid is dissolved in soda, and the solution treated in the cold with 3 per sodium amalgam; the yield is almost quantitative. When isocinnamic acid is treated with bromine in cold carbon bisulphide solution, it is converted into phenyl-$\alpha\beta$-bromopropionic acid (m. p. 196°); the yield is on the average 45—50 per cent. of the acid employed. Methyl isocinnamate, under the same conditions, is converted into methyl phenyl-$\alpha\beta$-bromopropionate (m. p. 117°). Isocinnamic acid is not changed when treated with iodine in cold carbon bisulphide solution, but on warming it is converted into cinnamic acid.

Isocinnamic acid dissolves almost completely in hydrobromic acid, and in about 24 hours it is completely converted into phenyl-β-bromopropionic acid (m. p. 137°); it is completely converted into phenyl-β-chloropropionic acid (m. p. 126°) when it is dissolved in a saturated solution of hydrogen chloride in glacial acetic acid and the solution kept for three to four days, whereas cinnamic acid under the same conditions is only very partially converted into the same additive compound.

Isocinnamic acid and cinnamic acid both require the same quantity (4 mols.) of potassium permanganate for complete oxidation to benzoic acid.

Isocinnamic acid occurs in storax; from about 2 kilos. of crude cinnamic acid from this source, the author isolated about 2 grams of pure isocinnamic acid by the method described above.

The relationship existing between cinnamic acid and isocinnamic acid can be explained by accepting Wislicenus' hypothesis; in accordance with this view, the acids would have the constitution $\begin{array}{r}Ph\cdot C\cdot H\\ \|\\ COOH\cdot C\cdot H\end{array}$ and $\begin{array}{l}Ph\cdot C\cdot H\\ \;\;\;\;\;\|\\ \;\;\;H\cdot C\cdot COOH\end{array}$ respectively.

The behaviour of isocinnamic acid is in complete accordance with the view that it is a labile form of cinnamic acid. F. S. K.

Benzallevulinic Acid and its Dibromide. By E. ERLENMEYER, Jun. (*Ber.*, **23**, 74—76).—This acid is best prepared as follows:— 11·6 grams of levulinic acid is dissolved in 200 grams of water, a solution of 8 grams of sodium hydroxide in 160 grams of water added, and the whole mixed with 10·2 grams of benzaldehyde and 100 grams of alcohol. The mixture is heated on the water-bath for about 20 minutes, then cooled, and the calculated quantity of hydrochloric acid added. The yield is about 50 per cent. of the theoretical. The

acid crystallises in quadratic scales or needles. *Benzallevulinic acid dibromide*, $C_{12}H_{12}O_3Br_2$, is readily formed when an acetic acid solution of bromine is added to an acetic acid solution of the acid. It crystallises in white prisms, which turn brown at about 150°, melts with decomposition at 153°, and dissolves in concentrated sulphuric acid with a yellow coloration which changes to bluish-green on warming.

L. T. T.

Coumarone in Coal Tar. By G. KRAEMER and A. SPILKER (*Ber.*, **23**, 78—83).—The authors have isolated considerable quantities of coumarone from coal tar. The fraction boiling between 168 and 175° was purified with caustic alkalis and by acids, and then treated gradually with bromine, care being taken not to let the temperature rise above 0°. *Coumarone dibromide*, $C_8H_6Br_2O$, is thus formed, and at 5° to 10° crystallises out in large, prismatic crystals melting at 88—89°. A kilo. of the tar fraction yields about 80 grams of coumarone dibromide. It is easily soluble in chloroform. When heated with alcoholic potash, *bromocoumarone*, C_8H_5BrO, is formed. This crystallises in prisms, melts at 39°, boils at 219—220°, and is volatile in steam. It is insoluble in water and dilute alkalis, soluble in organic solvents. When treated in alcoholic solution with sodium amalgam, coumarone, C_8H_6O, is gradually formed. This boils at 758 mm. pressure at 170—171° (uncorr.), and has a sp. gr. of 1·089 at 150°. It is resinified by concentrated sulphuric acid. The vapour-density determination by V. Meyer's method gave 118·4 (theory 118°). The above properties differ slightly from some of those given by Fittig, who probably only had very small quantities of the substance.

Coumarone dichloride, $C_8H_6Cl_2O$, was obtained by passing chlorine into a solution of coumarone in dry ether. It is a yellowish oil, boils at 245—248° with slight decomposition, and is volatile in steam, but even then slight separation of hydrogen chloride occurs. When treated with alcoholic potash, it yields *chlorocoumarone*, C_8H_5ClO, which crystallises in glistening prisms, melts at 74—75°, boils at 215—217°, and is volatile in steam.

No iodo-derivatives could be obtained, and coumarone was found to be very stable, distilling almost unchanged even when dropped on to fused potash, and being only very slightly decomposed when its vapour is passed through a red-hot tube. Oxidising agents cause complete decomposition. Strong mineral acids convert it into *paracoumarone*, a resinous substance easily soluble in ether, benzene, and chloroform, sparingly in alcohol, its solutions forming good varnishes owing to its stability towards acids and alkalis. A second solid and insoluble polymeride seems to be formed at the same time, and both seem to yield sulphonic acids when heated with strong sulphuric acid.

L. T. T.

Action of Benzamidine on Ethyl Acetylmalonate. By A. PINNER (*Ber.*, **23**, 161—166).—*Benzamidine benzamidylacetylmalonate*, NH:CPh·NH·CO·CHAc·COOH,NH_2·CPh:NH, separates in colourless crystals, when a mixture of benzamidine hydrochloride (2 mols.), a concentrated solution of potassium carbonate (1 mol.), and ethyl

acetylmalonate (1 mol.) is kept for some time at the ordinary temperature (compare this vol., p. 69). The crystals are washed with water, alcohol, and ether consecutively, and then repeatedly recrystallised from acetone in order to remove the ethyl phenylmethylhydroxypyrimidinecarboxylate which is also produced in the reaction. The pure product, when dried in the air, melts at 71°, and contains 1 mol. H_2O, which it loses over sulphuric acid. When heated gradually to 200°, it is converted into diphenylhydroxykyanidine with evolution of ammonia, carbonic anhydride, and acetone.

Diphenylhydroxykyanidine, $OH\cdot C\begin{smallmatrix}<N\cdot CPh>\\<N:CPh>\end{smallmatrix}N$, crystallises from alcohol or pyridine in colourless needles, melts at 289°, and is very sparingly soluble in alcohol and insoluble in water. It dissolves moderately easily in dilute soda, but is reprecipitated on the addition of concentrated soda or acids; it is also soluble in concentrated hydrochloric acid, but is reprecipitated on adding water.

F. S. K.

Action of Ethyl Sodiomalonate on Tribromotrinitrobenzene. By C. L. Jackson and G. D. Moore (*Amer. Chem. J.*, **12**, 7—21).—Tribromotrinitrobenzene was prepared by treating 20 grams of tribromodinitrobenzene with 500 c.c. of nitric acid of sp. gr. 1·52 and 200 c.c. of fuming sulphuric acid: a much better yield (40 per cent.) was obtained in this way than with the proportions recommended in an earlier paper. This tribromotrinitrobenzene was dissolved in benzene and treated with a slight excess of ethyl sodiomalonate; the liquid became dark-red in colour. It was allowed to remain for two or three days, and then treated with water and acidified with dilute sulphuric acid; this decomposed the red salt and liberated ethyl bromotrinitrophenylmalonate, which was extracted from the solution by means of ether and recrystallised from hot alcohol. The yield varied from 50 to 60 per cent.

Ethyl bromotrinitrophenylmalonate,

$$C_6HBr(NO_2)_3\cdot CH(COOEt)_2\ [= 3 : 2 : 4 : 6 : 1],$$

crystallises in slender, white needles arranged in radiating groups, and melts at 104—105°, becoming red and giving off gas at 160°. It is but slightly soluble in water, light petroleum, and ether, and in cold ethyl or methyl alcohol, but dissolves freely in these last two substances when hot, as also in benzene, carbon bisulphide, glacial acetic acid, chloroform, and acetone. It dissolves in potash, soda, or ammonia, giving red solutions, and the solution in ammonia forms reddish precipitates with the salts of many metals. The *sodium*-derivative, $C_6HBr(NO_2)_3\cdot CNa(COOEt)_2$, was prepared, and also a *copper*-derivative, which was found to explode when heated. All the salts seem to decompose rather easily. The ethereal salt itself, when boiled with dilute sulphuric acid, loses 2 mols. of carbonic anhydride, and forms a bromotrinitrotoluene shown by Bentley and Warren (this vol., p. 484) to have the formula [$Me : Br : (NO_2)_3 = 1 : 3 : 2 : 4 : 6$]. This, as well as its formation from symmetrical tribromotrinitrobenzene, shows that ethyl bromotrinitrophenylmalonate has the formula assigned to it

above. The action of nitric acid on it gives rise to at least two different substances, but these have not yet been fully investigated.

It is shown that the action of ethyl sodiomalonate on tribromotrinitrobenzene is represented by the following equations, all the bromine being eliminated as sodium bromide, and ethyl acetylenetetracarboxylate being formed:—

$$
\begin{aligned}
&C_6Br_3(NO_2)_3 + 3CHNa(COOEt)_2,\\
&\quad = C_6Br_2(NO_2)_3{\cdot}CH(COOEt)_2 + NaBr + 2CHNa(COOEt)_2\\
&\quad = C_6Br_2(NO_2)_3{\cdot}CNa(COOEt)_2 + CH_2(COOEt)_2 + CHNa(COOEt)_2 + NaBr\\
&\quad = C_6HBr(NO_2)_3{\cdot}CNa(COOEt)_2 + CHBr(COOEt)_2 + CHNa(COOEt)_2 + NaBr\\
&\quad = C_6HBr(NO_2)_3{\cdot}CNa(COOEt)_2 + C_2H_2(COOEt)_4 + 2NaBr.
\end{aligned}
$$

Ethyl trinitrophenylenedimalonate, $C_6H(NO_2)_3[CH(COOEt)_2]_2$, is formed by the further action of ethyl sodiomalonate on ethyl bromotrinitrophenylmalonate. It crystallises in long prisms melting at 123°, and resembling ethyl bromotrinitromalonate in solubility. It dissolves slightly in potash and soda, readily in ammonia, is not acted on by sulphuric or hydrochloric acid, but with nitric acid behaves in a similar manner to the bromotrinitrophenylmalonate.

C. F. B.

Metaxylylmalonic Acid. By O. POPPE (*Ber.*, **23**, 108—113).—*Ethyl metaxylylmalonate*, $C_6H_4Me{\cdot}CH_2{\cdot}CH(COOEt)_2$, is obtained, together with ethyl metadixylylmalonate, when metaxylyl bromide is treated with ethyl sodiomalonate; it is a thick, colourless oil boiling at 320° (250°; 150 mm.). The corresponding *methyl* salt,

$$C_6H_4Me{\cdot}CH_2{\cdot}CH(COOMe)_2,$$

is a colourless liquid boiling at about 300°.

Metaxylylmalonic acid, $C_{11}H_{12}O_4$, separates from a mixture of benzene and light petroleum in rhombic crystals, melts at 133° with evolution of carbonic anhydride, and is soluble in benzene, ether, and chloroform, but only sparingly in water and light petroleum. The *potassium* salt crystallises in slender needles, and is very hygroscopic. The *silver* salt and the *lead* salt are colourless, the *copper* salt is green.

Ethyl metaxylylmalonamate, $C_6H_4Me{\cdot}CH_2{\cdot}CH(CONH_2){\cdot}COOEt$, prepared by heating ethyl metaxylylmalonate with alcoholic ammonia at 150°, crystallises from alcohol or benzene in microscopic needles, and melts at 184—186°; when treated with water, it is converted into the *ethyl ammonium* salt, $C_{13}H_{19}O_4N$, which crystallises from alcohol in needles and melts at 77°.

Ethyl metaxylylmalonmethylamate,

$$C_6H_4Me{\cdot}CH_2{\cdot}CH(CO{\cdot}NHMe){\cdot}COOEt,$$

prepared by heating ethyl metaxylylmalonate with a 33 per cent. solution of methylamine at 150°, crystallises from alcohol in microscopic needles, and melts at 118—120°.

Metaxylylmalonanilide, $C_6H_4Me{\cdot}CH_2{\cdot}CH(CO{\cdot}NHPh)_2$, crystallises from benzene or alcohol in needles melting at 188°.

Metaxylylacetic acid, $C_6H_4Me{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is formed when metaxylylmalonic acid is heated at 133°; it could not be obtained in a crystalline condition. The *silver* salt has the composition $C_{10}H_{11}O_2Ag$.

Ethyl metaxylylchloromalonate, $C_6H_4Me{\cdot}CH_2{\cdot}CCl(COOEt)_2$, prepared by treating ethyl sodiochloromalonate with xylyl bromide, or by treating ethyl xylylmalonate with chlorine at about 200°, is a colourless liquid boiling at 260° (150 mm.).

Metaxylyltartronic acid, $C_6H_4Me{\cdot}CH_2{\cdot}C(OH)(COOH)_2$, is formed when the preceding compound is boiled with alcoholic potash: the acid cannot be isolated, as it immediately decomposes with evolution of carbonic anhydride. The *calcium* salt has the composition $C_{11}H_{10}O_5Ca$.

Metaxylylglycollic acid, $C_6H_4Me{\cdot}CH_2{\cdot}CH(OH){\cdot}COOH$, is a syrup; the *calcium* salt has the composition $(C_{10}H_{11}O_3)_2Ca$. F. S. K.

Experiments to Determine the Constitution of Tautomeric Compounds. By H. GOLDSCHMIDT and A. MEISSLER (*Ber.*, **23**, 253—280).—The methods hitherto employed for determining the constitution of tautomeric compounds do not, as is well known, give trustworthy results, because the reagents employed in forming the alkyl, acetyl, or metallic derivative may themselves bring about intramolecular change. The phenomena of intramolecular change can be explained in most, if not in all cases, by assuming that in the reactions of tautomeric compounds which take place under the influence of electrolytes, the intramolecular change is brought about by the free ions. If, then, the constitution of a tautomeric compound is to be ascertained experimentally, solutions of electrolytes must be excluded.

Starting from this point of view, the authors have studied the action of phenylcarbimide on a number of tautomeric compounds; in their opinion, the presence or absence of hydroxyl-groups is shown by the formation or non-formation of a carbanilido-derivative.

Ethyl succinylsuccinate and ethyl quinonedihydrodicarboxylate do not react with phenylcarbimide under the most varied conditions, a fact which seems to show that both compounds are diketo- and not hydroxy-derivatives.

Ethyl dicarbanilidodichlorohydroquinonedicarboxylate,

$$C_6Cl_2(O{\cdot}CO{\cdot}NHPh)_2(COOEt)_2,$$

is formed in small quantity when ethyl dichlorohydroquinonedicarboxylate (1 mol.) is heated for several hours with phenylcarbimide (2 mols.) and a little benzene at 150°. In absence of benzene the reaction takes place at 100°, but in presence of a large quantity of benzene no reaction takes place even at 200°, as the carbanilido-compound is decomposed by benzene at this temperature. It is a colourless, crystalline powder, melts at 195°, and is decomposed by soda, yielding aniline and the hydrate of dichlorohydroquinonedicarboxylic acid. The formation of this carbanilido-derivative shows

that ethyl dichlorohydroquinonedicarboxylate is not a quinone, but a hydroxy-derivative of benzene; its formation in benzene solution proves that Hantzsch and Herrmann's assumption (compare *Ber.*, **20**, 2801), that the green solutions contain a tautomeric quinone-derivative, is not correct.

Ethyl dicarbanilidodibromohydroquinonedicarboxylate,

$$C_6Br_2(O{\cdot}CO{\cdot}NHPh)_2(COOEt)_2,$$

is formed in small quantities when ethyl dibromohydroquinonedicarboxylate is heated at 140° with phenylcarbimide and a little benzene or light petroleum; it is a colourless, crystalline compound melting at about 200°. The conditions of formation are the same as in the case of the corresponding chloro-compound, as this carbanilido-derivative is also decomposed by benzene at 200°.

Phenylcarbimide has no action on ethyl dihydroxyquinonedicarboxylate (Hantzsch and Löwy, Abstr., 1886, 354) or on dihydroxyquinone.

Ethyl tetracarbanilidotetrahydroxyterephthalate,

$$C(O{\cdot}CO{\cdot}NHPh)_4(COOEt)_2,$$

is obtained when ethyl tetrahydroxyterephthalate is heated at 170° with phenylcarbimide and a little chloroform. It is an orange, crystalline powder, melts at 258—260°, and is insoluble in most ordinary solvents; it is decomposed by boiling soda. Attempts to prepare a dicarbanilido-derivative were unsuccessful. This behaviour shows that ethyl tetrahydroxyterephthalate contains four hydroxy-groups, all of which react with the same readiness.

Tricarbanilidophloroglucinol, $C_6H_3(O{\cdot}CO{\cdot}NHPh)_3$, is obtained when phloroglucinol is heated at 200° with phenylcarbimide and a little benzene. It separates from a mixture of benzene and light petroleum as a yellowish powder, and melts at 123°.

Ethyl tricarbanilidophloroglucinoltricarboxylate,

$$C(O{\cdot}CO{\cdot}NHPh)_3(COOEt)_3,$$

obtained from ethyl phloroglucinoltricarboxylate in like manner, separates from a mixture of benzene and light petroleum as a yellowish powder, begins to decompose at 155° and melts at 195°; it is decomposed by boiling soda, yielding phloroglucinol, aniline, and carbonic anhydride.

When ethyl mercaptan is heated with phenylcarbimide at 100°, ethyl phenylthiocarbamate, $NHPh{\cdot}CO{\cdot}SEt$, is formed, a fact which shows that the hydrosulphuryl-group behaves like the hydroxyl-group with phenylcarbimide.

Diphenylcarbamide and phenylthiocarbimide are formed when thiocarbanilide is heated at 180° for several hours with phenylcarbimide and a little benzene. Thiocarbanilide and paratolylcarbimide, under the same conditions, yield paratolylphenylcarbamide and phenylthiocarbimide. These experiments show that thiocarbanilide does not combine with phenylcarbimide, from which fact it may be assumed that thiocarbanilide has the constitution $CS(NHPh)_2$.

When $\alpha\alpha'$-lutidone is heated with phenylcarbimide and a little

benzene at 150°, carbonic anhydride is evolved, and phenylamidolutidine, identical with the compound obtained by Conrad and Epstein (Abstr., 1887, 501) from γ-chlorolutidine and aniline, is formed.

α-Quinolyldiphenylcarbamide, $C_{22}H_{17}N_3O$, is formed in small quantities with evolution of carbonic anhydride, when carbostyril is heated at 220° with phenylcarbimide and a little benzene. It crystallises from benzene in small, colourless needles, and melts at 150°. It is decomposed by concentrated hydrochloric acid at 200° yielding carbonic anhydride, aniline, and phenylquinolineamine, identical with the compound obtained by Friedländer and Weinberg (Abstr., 1885, 989) from α-chloroquinoline and aniline. These experiments seem to show that lutidone and carbostyril are analogously constituted.

F. S. K.

Sulphoncyanamides. By P. HEBENSTREIT (*J. pr. Chem.* [2], **41**, 97—120).—*Sodium benzenesulphoncyanamide*, $C_6H_5 \cdot SO_2 \cdot NNa \cdot CN$, is made by acting on benzenesulphonic chloride with sodium cyanamide; the latter is suspended in acetone (7—8 parts), and the chloride added by degrees, the reaction being completed on the water-bath, and the new substance afterwards precipitated by ether; the yield was 54 grams, theoretically 61 grams. It forms small, white needles (with 1 mol. H_2O) which decompose at 140°, and are soluble in alcohol and water, but not in benzene. It is also obtained by the action of cyanamide on benzenesulphonic chloride in aqueous soda solution, but not by the action of cyanamide and sodium ethoxide on benzenesulphonic chloride. The *silver* compound, the *barium* compound (with 1 mol. H_2O), and the *lead* compound (with 2 mols. H_2O) are described. *Benzenesulphoncyanamide*, $SO_2Ph \cdot NH \cdot CN$, obtained by the action of hydrochloric acid on the silver compound, crystallises in needles (with 1 mol. H_2O) which melt with decomposition at 158°, are sparingly soluble in cold water, chloroform, and benzene, insoluble in ether, and soluble in alcohol and acetone; the aqueous solution is strongly acid.

Sodium-α-naphthalenesulphoncyanamide, $C_{10}H_7^{\alpha} \cdot SO_2 \cdot NNa \cdot CN$, is prepared by suspending sodium cyanamide (8 grams) in ether (200 c.c.), adding α-naphthalenesulphonic chloride (14 grams), and heating on the water-bath for 24 hours, when the new substance remains as a white powder. It crystallises in lustrous, anhydrous leaflets, sparingly soluble in hot alcohol, easily soluble in acetone, and insoluble in ether. The *silver*, *lead*, and *barium* compounds have been obtained. *α-Naphthalenesulphoncyanamide*, obtained by decomposing the silver compound with hydrochloric acid, or the sodium compound with sulphuric acid, crystallises in white needles (with 1 mol. H_2O), decomposes at 115°, and is sparingly soluble in water to an acid solution, more freely soluble in alcohol, and insoluble in ether.

Sodium β-naphthalenesulphoncyanamide is similarly obtained; it crystallises in brilliant leaflets (with 2 mols. H_2O) of the same solubility as the α-compound. The *silver* compound, *barium* compound (with 2 mols. H_2O), and *lead* compound are described. *β-Naphthalenesulphoncyanamide* crystallises (with 1 mol. H_2O) in needles

which decompose at 120°, and are soluble in hot alcohol, but insoluble in ether.

Sodium ethylsulphoncyanamide, $SO_2Et\cdot NNa\cdot CN$, is prepared by adding sodium cyanamide (1 mol.) to a solution of sodium hydroxide (1 mol.), and mixing it with ethylsulphonic chloride (1 mol.); the water is evaporated, the residue dissolved in alcohol and precipitated by ether. It crystallises in long, silky needles (with 1 mol. H_2O) which melt at 88°, and are soluble in water, and alcohol sparingly in acetone and glacial acetic acid, but insoluble in ether. The *silver*, *lead*, and *barium* compounds are described. *Ethylsulphoncyanamide* forms anhydrous crystals which melt at 134°, and are freely soluble in hot alcohol, but only sparingly in cold water, and insoluble in ether.

When benzene- and α-naphthalenesulphoncyanamides are heated to 115° and 95° respectively, they decompose, forming benzenesulphonamide and α-naphthalenesulphonamide respectively, which sublime, and cyanuric acid, which is left in the residue of still undecomposed cyanamide. A. G. B.

Nitrotoluidinesulphonic Acids. By R. Nietzki and B. Pollini (*Ber.*, **23**, 138—140).—*Nitrotoluidinesulphonic acid*

$$[NH_2 : NO_2 : SO_3H : Me = 1 : 2 : 4 : 6]$$

can be prepared by nitrating acetyltoluidinesulphonic acid

$$[NHAc : Me : SO_3H = 1 : 2 : 4]$$

in sulphuric acid solution as previously described (compare Nietzki and Benckiser, Abstr., 1885, 535). It can also be obtained by dissolving orthacetotoluidide in fuming sulphuric acid, diluting with concentrated sulphuric acid, and then nitrating the product. It is best purified in both cases by converting it first into the barium salt, and then into the potassium salt. It crystallises in light-yellow needles. The *potassium* salt crystallises in orange needles, and is readily soluble in water, but only moderately easily in potash; when heated with dilute (1 : 1) sulphuric acid at 170—180° for about three hours, and the product treated with ammonia, nitrotoluidine $[NH_2 : NO_2 : Me = 1 : 2 : 6]$ is obtained. The acid yields a sparingly soluble, very explosive diazo-compound, which can be combined with phenols to form azo-dyes.

Diamidotoluenesulphonic acid, $SO_3H\cdot C_6H_2Me(NH_2)_2$, prepared by reducing the nitramido-acid with stannous chloride and hydrochloric acid, crystallises from water in colourless needles, and combines readily with orthodiketones, yielding azine-derivatives. The *azine* obtained with croconic acid forms a potassium salt which crystallises in almost black needles, and has the composition

$$C_5H_2O_3{<}\overset{N}{\underset{N}{|}}{>}C_6H_2Me\cdot SO_3K + H_2O.$$

Nitrotoluidinesulphonic acid $[NH_2 : NO_2 : Me : SO_3H = 1 : 2 : 4 : 6]$ can be obtained from paratoluidinesulphonic acid $[NH_2 : Me : SO_3H = 1 : 4 : 6]$, as described above; when paratoluidinesulphonic acid

[$NH_2 : SO_3H : Me = 1 : 3 : 4$] is treated in like manner, it yields a nitrotoluidinesulphonic acid [$NH_2 : NO_2 : SO_3H : Me = 1 : 2 : 3 : 4$]. Both compounds can be decomposed into nitrotoluidine

$$[NH_2 : NO_2 : Me = 1 : 2 : 4],$$

and on reduction they both yield diamido-compounds analogous to that described above. F. S. K.

Normal Propylbenzenesulphonic Acids. By A. CLAUS and O. WELZEL (*J. pr. Chem.* [2], **41**, 152—158).—α- and β-Propylbenzenesulphonic acids are propylbenzeneorthosulphonic and parasulphonic acids respectively; the authors doubt if Paternò and Spica (Abstr., 1877, 707) really obtained the latter, as the salts described by these chemists have properties differing from those now obtained. When the product of the reaction (*loc. cit.*) is gradually diluted with water, the first crystallisation consists chiefly of the ortho-acid. To completely separate the two acids, they are converted into the nickel salts; that of the ortho-acid crystallises from its hot aqueous solution, whilst that of the para-acid does not.

Propylbenzeneorthosulphonic acid [$Pr : SO_3H = 2 : 3$] crystallises in needles or small prisms (with 1 mol. H_2O), very soluble in water and alcohol, insoluble in other solvents. The *nickel salt* and the *chloride* were obtained. The *amide*, $C_6H_4Pr{\cdot}SO_2NH_2$, formed from the chloride by the action of ammonia, crystallises from water in colourless needles, and from other solvents in pearly leaflets; both forms melt at 104·5—105° (uncorr.). When brominated, the acid yields *orthobromopropylbenzene*, a yellow oil which boils at 222° (uncorr.), and yields orthobromobenzoic acid when oxidised. The bromopropylbenzenesulphonic acids are being investigated.

Propylbenzeneparasulphonic acid [$Pr : SO_3H = 1 : 4$] crystallises in needles which are more soluble than the ortho-acid; its salts are also more soluble than those of the ortho-acid, but do not crystallise so well. The *amide* crystallises in pearly, flattened needles or leaflets melting at 109—110° and soluble in most solvents. By brominating the acid, *parabromopropylbenzene* is obtained as an oil boiling at 220° (uncorr.), and solidifying in the cold; it is converted into parabromobenzoic acid by oxidation. A. G. B.

Paratolylphenylketoxime. By K. AUWERS (*Ber.*, **23**, 399—403). —Paratolylphenylketoxime was first prepared by Beckmann and Wegerhoff in the usual manner (Abstr., 1889, 1067). In view of the fact that, according to Hantzsch and Werner's hypothesis (this vol., p. 348), two stereometric isomerides of this compound, having the formulæ $\begin{array}{c}C_7H_7{\cdot}C{\cdot}C_6H_5\\ \Vert\\ N{\cdot}OH\end{array}$ and $\begin{array}{c}C_7H_7{\cdot}C{\cdot}C_6H_5\\ \Vert\\ HO{\cdot}N\end{array}$, should exist, the author has endeavoured to obtain a second oxime by methods similar to those successfully employed in the case of benzil (Abstr., 1888, 549, 597). In all cases, however, the result has been negative, the raw product obtained in each case being identical. This invariably contained an impurity, which could be removed by repeated crystallisation from alcohol, benzene, or light petroleum, the melting point being

finally found to be 153—154° instead of 140°, as given by Beckmann and Wegerhoff. That this impurity does not represent the second oxime is shown by the fact that acetic anhydride converts the crude product into the *acetyl*-derivative of paratolylphenylketoxime, $C_7H_7{\cdot}C_6H_5{\cdot}C{:}N{\cdot}OAc$, which is obtained quite pure by one recrystallisation from alcohol. It forms large lustrous prisms melting at 123—124°. It cannot be assumed that an intramolecular change of the second oxime by means of acetic anhydride takes place, as even the unstable benzil-γ-dioxime undergoes no such change with this reagent. The impurity is probably due to the unstable nature of the oxime, which decomposes, as already mentioned by Beckmann and Wegerhoff, even on remaining exposed to the air.

An attempt to bring about an intramolecular change in the oxime by treating it with alcohol at a high temperature likewise gave negative results. H. G. C.

Formation of Dibenzyl-derivatives. By O. Poppe (*Ber.*, **23**, 113—118).—*Ethyl cyanodiphenylsuccinate*,

$$COOEt{\cdot}CHPh{\cdot}CPh(CN){\cdot}COOEt,$$

is formed, together with ethyl diphenylsuccinate, when ethyl phenylchloracetate or ethyl phenylbromacetate is digested with an alcoholic solution of potassium cyanide (2 mols.), until the odour of hydrogen cyanide is no longer perceptible. (Compare Franchimont, this Journal, 1873, 390.) The solution is then extracted with ether, and the product repeatedly recrystallised; the yield is 4 per cent. of the ethyl salt employed. It separates from alcohol in prisms, melts at 105°, and is readily soluble in hot alcohol, ether, benzene, chloroform, and glacial acetic acid, but only sparingly in cold alcohol, and insoluble in water. When treated with sodium in alcoholic solution, it is converted into ethyl diphenylsuccinate. The corresponding *methyl* salt, $C_{19}H_{17}O_4N$, obtained in like manner from methyl phenylchloracetate, crystallises from alcohol in colourless plates, and melts at 101°. The *amyl* salt, $C_{27}H_{33}O_4N$, is an oil.

The compound $COOEt{\cdot}CHPh{\cdot}CPh(CONH_2){\cdot}COOEt$, is obtained when ethyl cyanodiphenylsuccinate is heated for a short time at 50—60° with concentrated sulphuric acid. It crystallises from a mixture of benzene and light petroleum in needles and melts at 157°. The free *acid*, $C_{17}H_{15}O_5N$, prepared by heating the ethyl salt at 100° with hydrochloric acid, crystallises from benzene and alcohol, melts at 190°, and is insoluble in water. When boiled with alcoholic potash, it is converted into diphenylsuccinic acid. F. S. K.

The Euxanthone Group. By C. Graebe (*Annalen*, **254**, 265—303; compare Abstr., 1887, 272; 1889, 886).—In this paper the author gives a more complete account of his investigations on euxanthone and its derivatives.

Piuri (purrée) or Indian-yellow is obtained in Bengal from the urine of cows which are fed exclusively on the leaves of the mango tree and water; the urine is heated, the precipitated dye separated and dried. The fact, observed by Kostanecki (Abstr., 1887, 272), that euxanthone

is converted into euxanthic acid in the animal organism, shows that mango-leaves contain some substance nearly related to euxanthone.

The author's analyses of very pure samples of piuri gave the following results in percentages:—Euxanthic acid, 51; silica and alumina, 1·5; magnesium, 4·2; calcium, 3·4; water and volatile substances, 39. His analyses differ from those of Stenhouse and Erdmann in showing the presence of considerable quantities of calcium. The poorer qualities contain a considerable quantity of euxanthone, partly in the free, partly in the combined state. The euxanthic acid and the euxanthone in piuri can be estimated and isolated as follows:—The dye is triturated with dilute hydrochloric acid until the whole has assumed the bright yellow colour of the free acid; it is then washed well with cold water to remove inorganic compounds, and the euxanthic acid extracted with a solution of ammonium carbonate; the residual euxanthone is dissolved in soda, reprecipitated with an acid, and dried at 100°.

Euxanthic acid melts at about 156—158°, but immediately afterwards begins to decompose, so that the melting point is difficult to observe. It forms two series of salts, of the composition $C_{19}H_{17}O_{11}M'$ and $C_{19}H_{16}O_{11}M'_2$ respectively. The magnesium salt, when dried in the air, has the composition $C_{19}H_{16}O_{11}Mg + 5H_2O$.

Accepting Schmiedeberg and Meyer's view of the constitution of glycuronic acid, the constitution of euxanthic acid may be expressed by the formula

$$OH{\cdot}C_6H_3{<}{}^{O-}_{CO}{>}C_6H_3{\cdot}O{\cdot}CH(OH){\cdot}[CH(OH)]_4{\cdot}COOH.$$

In accordance with this view, the decomposition of euxanthic acid into glycuronic acid and euxanthone may be represented by the equation $C_{19}H_{18}O_{11} = C_{13}H_8O_4 + C_6H_{10}O_7$.

In this decomposition the atomic complex $[CH(OH)]_2$ would be converted into the aldehyde-group, with elimination of 1 mol. H_2O, a view which would account for the fact that the decomposition of euxanthic acid takes place without the addition of the elements of water. The constitutional formula given above would also explain why euxanthic acid does not reduce Fehling's solution, whilst the liberated glycuronic acid does so. Glycuronic acid combines readily with phenylhydrazine; euxanthic acid, on the other hand, is not acted on even when heated with phenylhydrazine in alcoholic solution for two hours at 100°.

The hydroxyxanthone (m. p. 146°) prepared by Michael (Abstr., 1884, 310), by heating salicylic acid and resorcinol with zinc chloride, has the constitution $C_6H_4{<}{}^{O-}_{CO}{>}C_6H_3{\cdot}OH$ [O : OH = 2 : 6], this same compound can be prepared by heating salicylic acid and β-resorcylic acid with acetic anhydride. It is not acted on by hydroxylamine, or by phenylhydrazine, and when heated with zinc-dust it gives diphenylenemethane oxide (m. p. 100·5°). When fused with soda at 250—270° it is converted into trihydroxybenzophenone (m. p. 133°). This substance combines with phenylhydrazine, yielding a crystalline *hydrazone*, $OH{\cdot}C_6H_4{\cdot}C(N_2HPh){\cdot}C_6H_3(OH)_2$.

Erdmann's statement that euxanthone is converted into trinitroresorcinol (styphnic acid) by nitric acid is confirmed by the author's experiments; considerable quantities of oxalic acid are also formed in the reaction. When euxanthone is fused with soda or potash, it yields quinol, as previously observed by Baeyer, but resorcinol is also produced, and seemingly in about an equal quantity.

Euxanthone can be prepared by boiling a mixture of β-resorcylic acid (5 grams), hydroquinonecarboxylic acid (6 grams), and acetic anhydride (12 grams) for four hours in a small retort. The whole is then distilled, the neck of the retort being placed almost vertically, whereon, towards the end of the operation, most of the euxanthone sublimes. The acetic acid which passes over towards the end of the distillation is saturated with soda, and the solution treated with carbonic acid to precipitate the euxanthone; the sublimed euxanthone is dissolved in warm soda, and the filtered solution precipitated with carbonic anhydride; the yield of the pure product is 1 gram. Euxanthone prepared in this way melts at 240° (corr.), and is identical with the natural product (compare Abstr., 1889, 886). When it is warmed with water and sodium amalgam, the solution gradually becomes lighter in colour, and on adding an acid, a substance is precipitated which quickly turns violet on exposure to the air, and dissolves in concentrated sulphuric acid with an intense red coloration; this reaction is characteristic of the naturally occurring euxanthone. The *diacetyl*-derivative melts at 185°.

β-Isoeuxanthone, prepared from dinitroxanthone (m. p. 260°) gives a *diacetyl*-derivative which crystallises from alcohol in colourless needles melting at 175°. 3 : 6 Isoeuxanthone (m. p. 245—246°) prepared by Bistrzycki and Kostanecki, gives a *diacetyl*-derivative, $C_{13}H_6O_2(OAc)_2$, which melts at 124—130°. When isoeuxanthone is heated with potash and a little water, it is converted into an euxanthonic acid, which melts at about 200°, being reconverted into isoeuxanthone.
F. S. K.

ac.-Tetrahydro-β-naphthol and Secondary Closed Chain Alcohols. By E. Bamberger and W. Lodter (*Ber.*, **23**, 197—213).—*ac.-Tetrahydro-β-naphthol*, $C_{10}H_{11}\cdot OH$, is prepared by gradually adding 20 grams of sodium shavings in quantities of 4—5 grams to a boiling solution of 10 grams of β-naphthol in 200 grams of amyl alcohol, and heating until the whole is dissolved. The hot solution is poured into water and the alcoholic layer separated, washed several times with aqueous soda to remove as much ar.-tetrahydro-β-naphthol and unattacked β-naphthol as possible, then with water, and finally with dilute hydrochloric acid, and distilled under the ordinary atmospheric pressure until the temperature rises to 150—160°; the distillation at higher temperatures being conducted in a vacuum. The fraction boiling at 160—205° under a pressure of 40 mm. is a viscid, orange-yellow oil, and contains the whole of the "alicyclic" derivative together with noteworthy quantities of ar.-tetrahydro-β-naphthol and β-naphthol. The β-naphthol and the greater portion of the "aromatic" derivative can be removed by mixing the fraction with 15 per cent. aqueous soda and steam-distilling until the distillate

dissolves completely in aqueous soda. The oily ac.-tetrahydro-β-naphthol is extracted from the distillate by ether, and freed from the last traces of the "aromatic" derivative by treatment with a solution of diazotised sulphanilic acid in aqueous sodium carbonate; this converts the latter derivative into an azo-dye insoluble in ether, but is without action on the former. The yield amounts to about 30 per cent. by weight of the β-naphthol employed. ac.-Tetrahydro-β-naphthol is a colourless, transparent, extremely viscid, non-fluorescent oil with an odour resembling that of sage, it boils without decomposition at 264° under a pressure of 716 mm., and at 176·5—178° under a pressure of 53 mm. It is very slightly soluble in water, readily soluble in alcohol, ether, benzene, carbon bisulphide, and chloroform, and insoluble in alkalis. It does not react with diazo-compounds, and like ac.-tetrahydro-β-naphthylamine (Abstr., 1888, 712), yields hydrocinnamorthocarboxylic acid on oxidation. On treating its ethereal solution with sodium, hydrogen is evolved and the compound is converted into the sodium-derivative, behaving therefore like an alcohol under similar conditions. When warmed with solid potassium hydroxide, it readily yields dihydronaphthalene with the elimination of water.

Sodium ac.-tetrahydro-β-naphthyl carbonate, $C_{10}H_{11}O \cdot CO \cdot ONa$, is formed by passing carbonic anhydride through a well-cooled ethereal solution of the sodium-derivative of the hydronaphthol. It is a white, gelatinous, very unstable compound, undergoing decomposition on exposure to moist air. Acids decompose it at once with the evolution of carbonic anhydride and separation of the hydronaphthol.

ac.-Tetrahydro-β-naphthyl acetate, $CH_3 \cdot CO \cdot OC_{10}H_{11}$, is obtained by heating the hydronaphthol either with 3—4 times the quantity of acetic acid for some hours at 140—150°, or, better, with acetic anhydride, to which some fused sodium acetate has been added. It is a pale-yellow, extremely viscid oil with a fruity odour, and boils at 169° under a pressure of 34 mm. When distilled under atmospheric pressure, it boils at 268—280°, with partial decomposition into acetic acid and dihydronaphthalene.

ac.-Tetrahydro-β-naphthyl benzoate, $COPh \cdot OC_{10}H_{11}$, prepared by heating the hydronaphthol with benzoic acid at 170° for 48 hours, crystallises from alcohol in well-formed, lustrous tablets, melts at 62—63°, boils at 254—255° under a pressure of 40 mm., but decomposes partially into dihydronaphthalene and benzoic acid when distilled under atmospheric pressure; it is readily soluble in benzene, chloroform and warm alcohol, sparingly soluble in hot light petroleum.

ac.-Tetrahydro-β-naphthyl chloride, $C_{10}H_{11}Cl$, is obtained by warming the hydronaphthol with about 10 times its weight of concentrated hydrochloric acid. It was not, however, found possible to purify the product by distillation, since it decomposes on heating into dihydronaphthalene and hydrogen chloride. When ac.-tetrahydro-β-naphthol is treated at the ordinary temperature with colourless, fuming hydriodic acid (sp. gr. = 1·9), an oil is obtained which seems to be the corresponding *iodide*, but like the chloride it decomposes on distillation with the elimination of hydrogen iodide.

ac.-Tetrahydro-β-naphthyl phenylcarbamate, $NHPh \cdot CO \cdot OC_{10}H_{11}$, formed by treating the hydronaphthol with phenyl cyanate at the

ordinary temperature, crystallises in tufts of silky needles, melts at 98·5°, and is readily soluble in ether, benzene, chloroform, and boiling light petroleum.

Sodium ac.-tetrahydro-β-naphthylxanthate, $C_{10}H_{11}O·CS·SNa$, is readily prepared by treating the ethereal solution of the sodium derivative of the hydronaphthol with carbon bisulphide, and forms an ochre-yellow mass which dissolves readily in water and closely resembles sodium ethylxanthate in properties. From the aqueous solution, copper sulphate precipitates the brownish-black cupric salt, and this, like cupric ethylxanthate, slowly undergoes change into the ochre-yellow *cuprous* salt, $C_{10}H_{11}O·CS·SCu$, which crystallises from carbon bisulphide in bright-yellow crusts.

ac.-Tetrahydro-β-naphthol, like borneol and menthol, gives the reaction, therefore, of a true secondary alcohol, and a comparison of the properties of the three compounds makes it evident that hydroxyl-radicles can assume alcoholic functions not only in open but also, under certain conditions, in closed chain compounds. Like ac.-tetrahydro-β-naphthol, borneol and menthol (compare Arth, Abstr., 1886, 892) form chlorides which readily decompose into hydrogen chloride and camphene and menthene respectively, both readily eliminate water with the formation of camphene and menthene respectively, both yield xanthic acids resembling ethylxanthic acid in properties (compare Bamberger and Lodter, this vol., p. 516), and menthol benzoate decomposes partially into menthene and benzoic acid on distillation. It is noted that the oxidation-products of these three compounds—hydrocinnamorthocarboxylic acid, camphoric acid, and oxymenthylic acid respectively—contain the same number of carbon-atoms as the substances from which they are derived, thus differing from those of open chain secondary alcohols; such a difference, however, is only to be expected in the case of closed chain secondary alcohols. It is especially noteworthy that the products of partial oxidation in both closed and open chain secondary alcohols are ketones: borneol and menthol are known to give camphor and menthone on oxidation, and the authors have obtained evidence which points to the formation of an unstable ketone when ac.-tetrahydro-β-naphthol is oxidised by means of potassium dichromate and sulphuric acid, since, in addition to phthalic acid and hydrocinnamorthocarboxylic acid, a neutral oil is formed in small quantity which is readily volatile with steam and yields a well crystallised, nitrogenous compound on treatment with phenylhydrazine. W. P. W.

ar.-Tetrahydro-α-naphthol. By E. BAMBERGER and F. BORDT (*Ber.*, **23**, 215—218).—*ar.-Tetrahydro-α-naphthol*, $C_{10}H_{11}·OH$, is obtained as the sole product when α-naphthol in amyl alcohol solution is reduced with sodium, and is isolated by pouring the amyl alcohol solution into water, separating the alcoholic layer which contains the greater part of the product in the form of sodium salt, distilling off the alcohol, dissolving the yellowish-brown residue in water, acidifying, and extracting with ether; the ether is then removed by distillation and the resulting tetrahydro-α-naphthol purified by distillation under the ordinary pressure. It crystallises in silvery white tables re-

sembling naphthalene in appearance, melts at 68·5—69°, boils at 264·5—265·5° under a pressure of 705 mm. and is therefore identical with the product obtained from ar.-tetrahydro-α-naphthylamine by the diazo-reaction (compare Bamberger and Althausse, Abstr., 1888, 960). Adipic acid could not be obtained by oxidising the compound; cautious oxidation with potassium permanganate resulted only in the formation of oxalic and phthalic acids. On ethylation, it yields *ar-tetrahydro-α-ethoxynaphthalene*, $C_{10}H_{11}\cdot OEt$, a viscid, heavy oil which distils at 259° under a pressure of 705 mm. and has a pleasant odour.

Phenylazo-ar.-tetrahydro-α-naphthol, $N_2Ph\cdot C_{10}H_{10}\cdot OH$, prepared by the action of diazobenzene chloride on ar.-terahydro-α-naphthol in alkaline solution, crystallises from alcohol in beautiful, cantharides-green tablets showing a metallic lustre, and is insoluble in water, sparingly soluble in benzene, soluble in acetic acid, and readily soluble in chloroform.

Sulphophenylazo-ar.-tetrahydro-α-naphthol, $SO_3H\cdot C_6H_4\cdot N_2\cdot C_{10}H_{10}\cdot OH$, forms scarlet-red flocks. The sodium salt crystallises in orange-red scales showing a bronze lustre. W. P. W.

Derivatives of Nitro-β-naphthaquinone. By R. ZAERTLING (*Ber.*, **23**, 175—180).—*Nitronaphthaphenazine*, $C_6H_4{:}N_2{:}C_{10}H_5\cdot NO_2$, is produced by treating nitro-β-naphthaquinone (1 mol. prop.) dissolved in acetic acid with a solution of orthophenylenediamine hydrochloride (1 mol. prop.) and sodium acetate (2 mol. prop.) in dilute acetic acid. It crystallises from a mixture of phenol and acetic acid in well-formed, greenish-yellow prisms, melts at 221—222°, and is sparingly soluble in alcohol, benzene, ether, and acetic acid, insoluble in light petroleum. It dissolves in concentrated sulphuric acid with a carmine-red colour, and is precipitated unchanged from the solution on addition of water. *Amidonaphthaphenazine*, $C_6H_4{:}N_2{:}C_{10}H_5\cdot NH_2$, is formed when the nitro-derivative is reduced by heating with alcoholic ammonium sulphide for 2 hours at 100°, and crystallises from aniline in small, dark brownish-red crystals which yield a cherry-red powder. It sublimes in woolly, carmine-red flocks consisting of microscopic hair-like needles, melts at 191°, and is sparingly soluble in alcohol and ether, more soluble in benzene, and readily soluble in boiling aniline and phenol; the solutions, unlike those of the majority of eurhodines, are destitute of fluorescence. Concentrated sulphuric acid dissolves it with a brown colour, and the solution becomes yellow on dilution with water. The hydrochloride is sparingly soluble in boiling water, and, like all the salts of the base, is yellow in colour.

Nitro-β-naphthaquinol, $NO_2\cdot C_{10}H_5(OH)_2$, is best prepared from the quinone by reduction with stannous chloride and hydrochloric acid (Groves, Trans., 1884, 299), the yield amounting to 95 per cent. of that theoretically possible. It can also be obtained by dissolving powdered nitro-β-naphthaquinone in a saturated aqueous solution of sulphurous anhydride, and concentrating the solution on a water-bath to the crystallising point; the yield by this method, however, amounts only to about 60 per cent. of the theoretical, owing to the

carbonisation which occurs in concentrated solutions by the action of the sulphuric acid formed in the reduction. In view of the fact that nitro-β-naphthaquinol is almost insoluble in water, and that ether extracts nothing from the orange-red sulphurous acid solution, the author suggests that the quinol may combine either with sulphurous or sulphuric acid, forming a soluble compound which decomposes into its constituents when its solutions are concentrated. Nitro-β-naphthaquinol is also obtained on treating the quinone with phenylhydrazine, and in this reaction benzene, azobenzene, aniline, and nitrogen constitute the decomposition-products of the hydrazine. It sublimes in beautiful, long, red needles resembling sublimed alizarin in appearance, melts at 159·5°, is slightly volatile with steam, has an odour recalling that of juglone, and dissolves sparingly in boiling water. It is insoluble in cold concentrated sulphuric acid, but dissolves in aqueous alkalis forming deep-green solutions which, when shaken with air, become brighter in colour and cannot afterwards be precipitated by the addition of acids. Carbonic anhydride is eliminated when nitro-β-naphthaquinol is boiled in aqueous solution with barium or an alkaline carbonate. The quinol has feeble tinctorial powers, and with iron mordants gives yellowish-brown, with chromium mordants pale indigo-blue, and with aluminium mordants red colours which are not fast to soap.

Nitro-β-naphthaquinone reacts with hydroxylamine in the cold forming a pale-yellow, hygroscopic additive-compound,

$$NO_2\cdot C_{10}H_5O_2,NH_2\cdot OH,$$

which melts at 140—141° with decomposition, and decomposes into nitro-β-naphthaquinol with the evolution of nitrogen when boiled with acetic acid, phenol, alcohol, or water. W. P. W.

Di-β-naphthylketone Oxide. By A. Claus and W. Ruppel (*J. pr. Chem.* [2], **41**, 48—54).—*Di-β-naphthylketone oxide*, $CO\colon(C_{10}H_6)_2\colon O$, is obtained when ethylidene di-β-naphthyl oxide (Abstr., 1887, 271) is dissolved in boiling glacial acetic acid (10 grams in 150 grams), and a glacial acetic solution of chromic acid (15 grams in 100 grams) added thereto; after 10 minutes' heating, the mixture is cooled, when the oxide crystallises. It forms light-grey, silvery leaflets which melt at 149° (uncorr.), and sublime at a higher temperature in slender, colourless needles which soon become yellowish-grey; it dissolves in the usual solvents except water. It is not changed by concentrated hydrochloric acid or by alcoholic potash, and forms no compound with phenylhydrazine.

Dinitrodi-β-naphthylketone oxide, obtained by nitrating the above, is precipitated on adding water to its solution in strong acid as an amorphous powder which aggregates at 268°, and is insoluble in all solvents except nitrobenzene, from which it is precipitated by alcohol in leaflets melting at 275° (uncorr.). By reduction, it yields crystals of an amido-compound (?) melting at 182°.

Barium di-β-naphthylketoneoxidedisulphonate was obtained by sulphonating the oxide, &c.

Dibromodi-β-naphthylketone oxide crystallises in beautiful, lustrous

needles which melt at 181° (uncorr.), and are soluble in ether, acetone, and glacial acetic acid.

Methylene-di-β-naphthyl oxide, $CH_2\colon(C_{10}H_6)_2\colon O$, is the product of the reduction of the ketone oxide; it crystallises in small, lustrous, yellowish needles melting at 165° (uncorr.), and soluble in the usual solvents. When the reducing agent is concentrated hydriodic acid and the temperature 180°, a *dinaphthylmethane* is obtained: this forms glittering leaflets which melt at 137° (uncorr.), and are soluble in hot alcohol and ether; it is not identical with Richter's dinaphthylmethane (Abstr., 1881, 281). A. G. B.

Decomposition of ac.-1 : 4′-Tetrahydronaphthylenediamine into its Optically Active Components. By E. BAMBERGER (*Ber.*, **23**, 291—292).—The lævo-rotatory modification of ac.-1 : 4′-tetrahydronaphthylenediamine is obtained by concentrating an aqueous solution of the hydrogen tartrate of the optically inactive base to a thick syrup, and adding a minute fragment of conine dextrotartrate. Slender needles of the salt of the lævo-rotatory modification at once begin to crystallise out. The hydrochloride crystallises in transparent, compact, lustrous prisms, and in aqueous solution has a specific rotatory power of $[\alpha]_D = -7° 29' 50''$.

The hydrogen salt of the dextro-rotatory modification forms lustrous needles which crystallise with extreme slowness from the syrupy mother liquor. The hydrochloride in aqueous solution has a specific rotatory power of $[\alpha]_D = +8° 8' 49''$. W. P. W.

Homologues of Anthracene and Anthraquinone. By K. ELBS (*J. pr. Chem.* [2], **41**, 1—32 and 121—151).—This paper consists chiefly of descriptions of the preparation of the methylanthracenes and methylanthraquinones, together with their dicarboxylic acids, given in greater detail than heretofore (compare Abstr., 1885, 261; 1886, 461, 557; 1887, 841, 940).

β-Methylanthracene melts at 199—200° and β-methylanthraquinone (Abstr., 1886, 557, 1029) at 176—177°.

The *ammonium*, *calcium*, *lead*, and *silver* salts, and the *anhydride* both of 2 : 3-anthraquinonedicarboxylic acid and of 2 : 3-anthracenedicarboxylic acid are described; the salts are all anhydrous, amorphous precipitates.

When 1 : 3-dimethylanthracene is treated with bromine in carbon bisulphide, a crystalline *dibromo*-1 : 3-*dimethylanthracene* is produced; it melts at 175°—180° with decomposition.

"*Metadimethylanthracylene*" is the name given by the author to the hydrocarbon $C_{16}H_{12} = C_6H_4\colon C_2H{<}{\genfrac{}{}{0pt}{}{CH_2}{C_6H_2Me}}$ [$CH_2 : Me = 1 : 3$], obtained by reducing 1 : 3-dimethylanthraquinone with zinc-dust and ammonia (Abstr., 1887, 841). When treated with bromine, it yields a crystalline *dibromo-derivative*, $C_{16}H_{10}Br_2$, melting at 175°, soluble in acetone and in carbon bisulphide, and converted by nitric acid into 1 : 3-anthraquinonedicarboxylic acid, and by alcoholic potash into 1 : 3-*dimethylanthranol*; the latter crystallises in slender, colourless needles which melt at 155°.

The *ammonium*, *potassium*, *sodium*, *calcium*, *barium*, *lead*, *copper*, and *silver* salts, and the *chloride* of 1 : 3-anthraquinonedicarboxylic acid are described; as are also the *ammonium*, *copper*, and *silver* salts, and the *chloride* of 1 : 3-anthracenedicarboxylic acid.

1 : 4-Dimethylanthraquinone has been prepared by Gresly (Abstr., 1886, 1029); it melts at 118—119°. When reduced by zinc-dust and ammonia, it yields a hydrocarbon, $C_{16}H_{12}$ (compare above), which crystallises in leaflets melting at 63°, and gives a *picrate* which melts at 129°.

1 : 4-*Anthraquinonedicarboxylic acid*, obtained by oxidising 1 : 2-dimethylanthraquinone with nitric acid, forms crystals which are still solid at 300°, and are insoluble in water, but soluble in alcohol; its *alkali* salts, and its *calcium*, *lead*, and *silver* salts are described. 1 : 4-*Anthracenedicarboxylic acid*, obtained by reducing the preceding compound, separates from alcohol on dilution as a light-brown, crystalline powder melting at about 320°; its *alkali* salts and its *calcium*, *lead*, and *silver* salts are described.

1 : 2 : 4-Trimethylanthracene (Gresly, Abstr., 1886, 1029), when added to a solution of picric acid in benzene, forms a *picrate* which crystallises in brownish-red needles melting at 145°, and immediately decomposed by alcohol.

Gresly's method for obtaining 1 : 2 : 4-trimethylanthraquinone (*loc. cit.*) is best carried out as follows:—Pseudocumoylorthobenzoic acid (10 grams) is shaken with strong sulphuric acid (100 c.c.) and slowly heated to 115°, at which temperature it is kept for one hour; it is then cooled to 70—80° and phosphoric anhydride (10 grams) added, the temperature being again raised to 115—120° and kept there for two hours, after which the mixture is allowed to cool and poured into much water. The precipitated quinone is washed with cold water, hot aqueous soda solution, and hot water, dissolved in xylene, and precipitated by absolute alcohol. Thus obtained, it forms long, yellow needles which melt at 162—163° and sublime.

"*Trimethylanthracylene*," $C_{17}H_{14}$, $= C_6H_4{:}C_2H{<}\begin{smallmatrix}CH_2\\ |\\ C_6HMe_2\end{smallmatrix}$?, is obtained when 1 : 2 : 4-trimethylanthraquinone is reduced with zinc-dust and ammonia; it crystallises in colourless leaflets which melt at 64°. Its *picrate* forms dark-red needles melting at 134°. When brominated, it yields a *dibromo-derivative*, $C_{17}H_{12}Br_2$, which crystallises in yellow, transparent prisms melting at 105° with decomposition, and sparingly soluble in alcohol.

Anthraquinone-1 : 2 : 4-*tricarboxylic acid*, prepared by oxidising 1 : 2 : 4-trimethylanthraquinone with dilute nitric acid according to the method already given, crystallises in yellowish-white nodules not melting or decomposing at 320°, and soluble in alcohol, but nearly insoluble in water. The ammonium salt was not obtained pure, but the *monosodium salt* (with 2 mols. H_2O), the *disodium salt* (with 3 mols. H_2O), the *normal sodium salt*, and the *normal calcium*, *copper*, *lead*, and *silver salts* are described; the *ethyl salt* forms small, lustrous, yellow leaflets melting at 125°.

Anthracene-1 : 2 : 4-*tricarboxylic acid* is made by reducing the preceding acid with zinc-dust and ammonia; it is a deep yellow precipi-

tate, insoluble in water, but soluble in light petroleum, benzene, and alcohol; at 260° it yields a red sublimate, apparently an anhydride. The *alkali salts* and the *silver salt* have been obtained.

There are two *nitro*-1 : 2 : 4-*trimethylanthraquinones*, designated by the author as I and II.

I is obtained when 1 : 2 : 4-trimethylanthraquinone (5 grams) is dissolved in strong sulphuric acid (100 grams) at the ordinary temperature, and powdered potassium nitrate (2·2 grams) gradually added; the mixture is allowed to remain for some hours and then poured into much water. The nitro-derivative is thus separated as a red powder, freely soluble in boiling benzene and xylene, which deposit it as an impure, crystalline mass melting with decomposition at 195—200°. The corresponding *tricarboxylic acid* forms small crystals which melt with decomposition at 308—310°, and are soluble in most solvents except water; its three *sodium salts*, and its *neutral calcium*, *strontium*, *barium*, *nickel*, *cobalt*, *lead*, *copper*, and *silver* salts were obtained. The corresponding *amido-tricarboxylic acid* crystallises in small, dark-red leaflets melting at 210°, and soluble in hot water and in alcohol.

II is formed when 1 : 2 : 4-trimethylanthraquinone (5 grams) is dissolved in nitric acid of sp. gr. 1·52 (100 c.c.), cooled by ice, and, after six hours, poured into much water; it is a pale-red powder, soluble in glacial acetic acid, benzene, and xylene; it cannot be purified, and decomposes at 180°. The corresponding *tricarboxylic acid* forms a dubiously crystalline, red-yellow powder, soluble in alcohol and benzene, and melting with decomposition between 360° and 370°; its three *sodium salts*, its *calcium*, *barium*, *strontium*, *nickel*, *lead*, and *silver salts* were obtained; the *copper salt* forms red needles dissolving in ammonia with a red colour, whereas the copper salt of the I-tricarboxylic acid forms green needles soluble in ammonia with an emerald-green colour. The corresponding *amido-tricarboxylic acid* crystallises in deep-red leaflets melting at 255°, soluble in water and alcohol. The corresponding *amido-quinone* forms a red precipitate, which is obtained as a crystalline mass by decomposing its saturated alcoholic solution with water; it melts at 154—155°, and sublimes in slender, lustrous, dark-red needles.

Dinitro-1 : 2 : 4-*trimethylanthraquinone* is the ultimate product of the action of nitric acid (sp. gr. 1·54) on the above quinones; it is a dark-yellow powder, soluble in boiling glacial acetic acid, benzene, and xylene, and melting with decomposition between 240 and 260°. The corresponding *tricarboxylic acid* and its *silver salt* were obtained.

2 : 1′ : 4′-*Trimethylanthraquinone*, obtained by oxidising 2 : 1′ : 4′-trimethylanthracene (Abstr., 1887, 941) with chromic acid in glacial acetic solution, crystallises in yellow needles which melt at 184° and sublime; it dissolves sparingly in alcohol. When it is oxidised with chromic acid, a mixture of di- and tricarboxylic acids is produced; the *silver dicarboxylate* was obtained.

3 : 1′ : 3′-*Trimethylanthracene*, obtained by the condensation of dimetaxylyl ketone (Cosack, *Diss.*, *Freiburg i. B.*, 1889; compare Abstr., 1887, 941), melts at 222°, and is sparingly soluble in alcohol and light petroleum, but more freely in other solvents. When

brominated in carbon bisulphide solution, it yields *γ-dibromo-3 : 1′ : 3′-trimethylanthracene*, $C_6H_2Me_2\colon C_2Br_2\colon C_6H_3Me$, which crystallises in leaflets melting at 142°.

3 : 1′ : 3′-*Trimethylanthraquinone* crystallises in yellow needles melting at 190°, subliming and soluble in glacial acetic acid, and sparingly in alcohol; the corresponding *tricarboxylic acid* crystallises in yellow leaflets nearly insoluble in water and melting above 300°; its *ammonium* and *barium salts* are described.

Phenylbenzoylorthobenzoic acid, $COOH{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4Ph$, is obtained by heating diphenyl with phthalic anhydride in the presence of aluminium chloride in light petroleum (b. p. 90—100°); the petroleum is distilled off with steam, and the residue dissolved in weak soda solution and fractionally precipitated by hydrochloric acid; the flocks thus obtained are crystallised from alcohol, when only the first portions that come down are crystalline, the rest separating as flocks; the last portions, therefore, are dissolved in weak ammonia and converted into the copper salt by adding copper sulphate and evaporating off the ammonia; from the copper salt the acid is separated by hydrogen sulphide. It crystallises in small, yellowish-white needles melting at 225°, and is sparingly soluble in light petroleum, but soluble in other solvents. The *ammonium*, *nickel*, *copper*, *lead*, and *silver* salts are described, as are also the *sulphonic acid*-derivative and its *barium* salt.

When phenylbenzoylorthobenzoic acid is heated with zinc-dust and ammonia, *phenylbenzhydrylorthobenzoic lactone*,

$$CO{<}{}^{C_6H_4}_{-O-}{>}CH{\cdot}C_6H_4Ph,$$

is formed; it crystallises in colourless nodules, and melts at 204°; when heated to a higher temperature, a part sublimes, the sublimate melting at 205—206°; it is soluble in most solvents. By carrying the reduction still further, *phenylbenzylorthobenzoic acid*,

$$C_6H_4Ph{\cdot}CH_2{\cdot}C_6H_4{\cdot}COOH,$$

is obtained; it forms well-formed, colourless, or slightly red crystals which melt at 184—185° without decomposition, and are soluble in alcohol and in ether; the *silver salt* was obtained. A. G. B.

Truxene- and Truxone-derivatives. By C. LIEBERMANN and O. BERGAMI (*Ber.*, 23, 317—322; compare Abstr., 1889, 698, and Hausmann, *ibid.*, 1172).—The quinone-like compound obtained by oxidising truxene is identical with tribenzoylenebenzene (Gabriel and Michael, Abstr., 1878, 734). The molecular formula of truxone has not yet been ascertained, but it is probably a tribenzoylenehexahydrobenzene $(C_9H_6O)_3$.

When truxone is boiled with hydroxylamine in glacial acetic acid solution, it is gradually but completely converted into a colourless, insoluble powder which contains nitrogen; this compound is only very sparingly soluble in boiling alkalis, and is, probably, the anhydride of the oxime. When heated at 100° for a short time with concentrated sulphuric acid, it is converted into the *oxime*, which is

precipitated on adding water. The oxime is, however, unstable, and is almost completely reconverted into the anhydride when it is dried. The *acetyl*-derivative, $(C_9H_6{:}N{\cdot}OAc)_3$, can be obtained by boiling the oxime with acetic anhydride. It crystallises in small needles, melts at 261°, and is moderately easily soluble in glacial acetic acid; when boiled with alcoholic potash, or when heated at 100° with concentrated sulphuric acid, it is reconverted into the oxime.

Dihydrodiphenylenehydroxyanthraquinone,

$$CHPh<\begin{matrix}CH{:}C\\CH_2{\cdot}C\end{matrix}\geqslant CH - CO<\begin{matrix}C_6H_3 - \\ C_6H_2(OH)\end{matrix}>CO,$$

is formed when truxone is melted with potash (12—15 parts). When the resulting deep-blue mass is treated with a little water, a small quantity of a purple-red dye passes into solution. On boiling the residue with a large quantity of water, a deep-blue solution is obtained, and on acidifying, the hydroxy-quinone is precipitated. It crystallises from glacial acetic acid or acetic anhydride in slender, dirty-yellow needles, melts at 266°, and is only sparingly soluble in ether, alcohol, and benzene. It dissolves slowly in cold alkalis with a violet-blue coloration, and in concentrated sulphuric acid forming a greenish-yellow solution, from which it is precipitated unchanged on adding water. The *acetyl*-derivative, $C_{25}H_{18}O_4$, prepared by boiling the hydroxyquinone with acetic anhydride and sodium acetate, crystallises from benzene in needles, melts at 180°, and is moderately easily soluble in alcohol, benzene, and glacial acetic acid.

F. S. K.

Synthesis of Chrysene and Allied Hydrocarbons. By G. KRAEMER and A. SPILKER (*Ber.*, **23**, 84—87).—Klotz found that when the vapours of the higher boiling fractions of coal-tar were superheated, considerable quantities of chrysene were formed, but that neither mesitylene nor pseudocumene produced it when heated alone. He was, however, unable to continue his investigations, and the authors have therefore examined the action of heat on other constituents of coal-tar. They find that although neither coumarone nor naphthalene yield chrysene when heated alone, it is produced in considerable quantity when their mixed vapours are passed through a red-hot tube, water being formed at the same time. The reaction is represented by the equation

$$O<\begin{matrix}C_6H_4\\|\\C_2H_2\end{matrix} + C_{10}H_8 = C_{10}H_6<\begin{matrix}C_6H_4\\|\\C_2H_2\end{matrix} + H_2O.$$

Further experiments showed that the power of coumarone to condense with hydrocarbons is not confined to naphthalene. When the mixed vapours of benzene and coumarone are passed through a red-hot tube, phenanthrene is formed.

It is thus probable that coumarone may play an important part in the formation of many of the condensed hydrocarbons found in coal-tar.

L. T. T.

Researches on the Constitution of β-Nitrocamphor and of α-Chloronitrocamphor. By P. CAZENEUVE (*Bull. Soc. Chim.* [3], 2,

705—710).—The reduction of α-chloronitrocamphor by the zinc-copper couple yields α-nitrocamphor as the principal product, whereas reduction by sodium determines the formation of the β-derivative (compare Abstr., 1887, 842—970).

α-Chloronitrocamphor (100 grams) dissolved in boiling toluene (400 grams) is reduced with the theoretical amount of sodium, the precipitate formed is exhausted with alcohol, and from the solution silky needles of sodium β-nitrocamphorate separate on spontaneous evaporation of the solvent; these are identical with the product obtained from β-nitrocamphor, but differ from that yielded by α-nitrocamphor in producing an ochreous-red precipitate with ferric chloride, the α-derivative giving a blood-red coloration. An acetyl-derivative of this sodium salt exists. β-Nitrocamphor is formed by the action of hydrochloric acid on its sodium compound, and crystallises from light petroleum in white, badly-defined crystals, which melt at 83—84° (the melting point, 97°, previously given, being incorrect); it is perhaps identical with the nitrocamphor prepared by Schiff (Abstr., 1880, 891) from bromonitrocamphor.

β-Nitrocamphor differs from the α-derivative in giving Liebermann's reaction, and when it is treated with concentrated potash, potassium nitrite is formed; hence it appears to be a nitroso-derivative, $C_8H_{14}<\begin{matrix}C(OH)\cdot NO\\ | \\ CO\end{matrix}$, and the author thinks that it is formed by an intramolecular change from the α-compound, which is a nitro-derivative, $C_8H_{14}<\begin{matrix}CH\cdot NO_2\\ | \\ CO\end{matrix}$.

α-Chloronitrocamphor is probably a chloroxynitroso-derivative, as it also gives Liebermann's reaction with phenol and sulphuric acid, and when treated with potash lye yields potassium nitrite at a lower temperature than that at which potassium nitrate is reduced; again, when boiled in strong alcohol with finely-divided zinc, copper, or iron, the chlorine-atom is removed, as in the case of hexachlorophenol, and two isomeric zinc salts are produced corresponding with the general formulæ $C_8H_{14}<\begin{matrix}C(OM)\cdot NO\\ | \\ CO\end{matrix}$ and $C_8H_{14}<\begin{matrix}CM\cdot NO_2\\ | \\ CO\end{matrix}$.

T. G. N.

New Bases derived from Camphor: Camphamines. By P. Cazeneuve (*Bull. Soc. Chim.* [3], **2**, 715—717).—On heating α-chlorocamphor (5 grams) with saturated aqueous ammonia (20 grams) in sealed tubes at 180° for 24 hours, a black mass is formed; this is dissolved in acetic acid at 100°, and to the solution, after precipitation and filtration of the unaltered chlorocamphor by addition of water, an excess of potassium carbonate is added, and the precipitated base is extracted with ether.

The base is removed from its solution in ether by agitation with water acidified with hydrochloric acid, and is precipitated by aqueous ammonia, and after washing dried in a vacuum; the yield is about 2 per cent.

This camphamine, $C_{10}H_{15}O\cdot NH_2$, crystallises from light petroleum in radiating groups of needles, melts at 180°, and has the odour of

old tobacco; it is insoluble in water, but is soluble in alcohol, ether, and chloroform, and also in weak acids, from which its corresponding salts crystallise; the hydrochloride forms long, colourless needles. Unlike the base obtained from camphor by Schiff (Abstr., 1880, 892), this does not reduce Fehling's solution, and is unattacked by acetic chloride.

From the chlorocamphor obtained by acting on camphor with hypochlorous acid, an isomeric base may be obtained in like manner. This is not crystalline, and is unstable.

Both these bases are precipitated by the ordinary reagents for alkaloïds. T. G. N.

Camphoric Acid. By E. BAMBERGER (*Ber.*, **23**, 218—219).—Camphoric acid does not unite with hydrogen bromide even when heated at 120° with a solution saturated at 0°, and is only attacked with great difficulty by potassium permanganate. It cannot, therefore, contain any carbon-atoms united in the same manner as those of ethylene, and the author, therefore, believes the usually accepted formula of camphoric acid, $\begin{array}{l}CH_2\cdot CPr\cdot COOH\\ |\quad\quad |\\ CH_2\cdot CMe\cdot COOH\end{array}$, according to which it is a derivative of tetramethylene, to be correct. This corresponds with the formula $\begin{array}{l}CH_2\cdot CPr\cdot CH_2\\ |\quad\quad |\quad\quad |\\ CH_2\cdot CMe\cdot CO\end{array}$ for camphor. H. G. C.

Action of Carbon Bisulphide on Menthol and Borneol. By E. BAMBERGER and W. LODTER (*Ber.*, **23**, 213—215).—The resemblance which exists between both the camphor alcohols and the alicyclic β-tetrahydronaphthol has led the authors to examine the action of carbon bisulphide on menthol and borneol; the results obtained show that these alcohols likewise form xanthic acids.

Menthylxanthic acid, $C_{10}H_9O\cdot CSSH$. To obtain this compound, an ethereal solution of menthol is treated with fine slices of sodium until no more dissolves, the solution, which contains the sodium compound partly in suspension, is then separated from the excess of sodium, and carbon bisulphide added; after remaining for two hours, the greater part of the ether and unaltered carbon bisulphide is distilled off, and the residue shaken with water, which takes up the sodium salt of the menthylxanthic acid, unaltered menthol remaining dissolved in the ether. Copper sulphate solution precipitates a dark-brown amorphous *cupric* salt, which readily passes into the *cuprous* salt on warming. This is purified by washing with water and ether, dissolving in carbon bisulphide, evaporating off the greater part of the latter, and adding light petroleum. Thus obtained the cuprous salt forms a heavy, yellow, crystalline powder. The free acid is obtained from the sodium salt by the addition of mineral acids as an unstable oil, which readily decomposes with evolution of hydrogen sulphide.

Bornylxanthic acid, $C_{10}H_{17}O\cdot CSSH$, is obtained in a similar manner from borneol. Its cuprous salt is, like the corresponding menthyl-compound, a heavy, yellow, crystalline powder.

H. G. C.

Active and Inactive Bornyl Phenylcarbamates and Isobornyl Phenylcarbamates. By A. HALLER (*Compt. rend.*, **110**, 149—152).—Bornyl phenylcarbamates are obtained by the interaction at the ordinary temperature of phenyl isocyanate and a camphol in molecular proportion; the hard, compact, crystalline mass thus obtained is recrystallised from alcohol. All the bornyl phenylcarbamates form slender, white needles which dissolve in ether, benzene, and toluene, but are only slightly soluble in cold alcohol and in light petroleum. The melting point varies with the particular camphol from which they are derived. The rotatory powers and melting points are given in the following table:—

	Melting point.	$[\alpha]_D$.
Dextrogyrate α-bornyl phenylcarbamate...	137·75°	+34·22°
Lævogyrate α- „ „ ..	137·25	−34·79
Lævogyrate β- „ „ ..	130·05	−56·77
Racemic −α +α „ „ ..	140·00	—
Bornyl phenylcarbamate from inactive camphol +α −β....................	133·00	−7·50
Bornyl phenylcarbamate from inactive camphol −α +β....................	132·60	+7·32

The melting points and rotatory powers of analogous pairs are practically identical, but the rotatory power of the β-derivatives is higher than that of the isomeric α-derivatives, and as a consequence the phenylcarbamates from the inactive αβ-camphols are active. β-Bornyl phenylcarbamate, unlike β-borneol, has the same rotatory power in solution in benzene as in alcohol. It would seem that in the isocamphols, it is the asymmetrical group $:C\cdot CH<^{CH_2}_{OH}$ which is affected by the solvent, and that when this group enters into combination the influence of the solvent disappears. C. H. B.

Apiole. By J. GINSBERG (*Ber.*, **23**, 323—325; compare Abstr., 1888, 1206).—Aponic acid is formed when manganese dioxide (60 grams) is added, in small portions at a time, to a boiling mixture of concentrated sulphuric acid (60 grams), water (240 grams), and isoapiole (6 grams). The whole is boiled for four hours with frequent agitation, the boiling solution filtered, and the residue repeatedly extracted with boiling water; the acid is extracted from the concentrated filtrate with ether, and purified by dissolving it in ammonia and reprecipitating with an acid. It crystallises from boiling water, in which it is only sparingly soluble, in small, colourless needles, and melts at 252° with decomposition. It is almost insoluble in cold water, benzene, and light petroleum, and only sparingly in ether, but more readily in hot alcohol and carbon bisulphide; it dissolves in concentrated sulphuric acid forming a colourless solution, from which it is reprecipitated unchanged on adding water.

The composition of this acid is probably either $C_{14}H_{12}O_6$ or $C_{14}H_{10}O_6$.

Apiole does not give an oxidation-product under the conditions described above.

Aponic acid is not acted on by concentrated hydriodic acid or hydrochloric acid at 200°, and it undergoes no change when boiled for a long time with a mixture of nitric acid and concentrated sulphuric acid. Chromic acid, bromine, chlorine, phosphorous chloride, phosphoric chloride, phenylhydrazine, and hydroxylamine have no action on aponic acid. The *calcium* salt is a colourless, granular powder, sparingly soluble in cold but more readily soluble in boiling water. The *barium* salt separates from dilute alcohol in the form of a colourless, granular powder. The *silver* salt is colourless, and could not be obtained in a crystalline condition. The *ethyl* salt, prepared from the silver salt, crystallises from boiling water in long, slender needles, melts at 119—120°, and is moderately easily soluble in most ordinary solvents, but insoluble in alkalis. It dissolves in concentrated sulphuric acid, forming a colourless solution, but is reprecipitated unchanged on adding water; it is not acted on by phenylhydrazine or by hydroxylamine, but it seems to be decomposed by boiling water.

The analyses of the salts gave results which leave the composition of the acid undecided. F. S. K.

Diastase. By C. J. LINTNER and F. ECKHARDT (*J. pr. Chem.* [2], **41**, 91—96; compare Abstr., 1886, 386; 1887, 165; 1888, 497).—To settle whether malt diastase and the ferment of ungerminated grain are identical, it is necessary to compare their action on starch, both as to the most favourable temperature and the quantity of sugar produced (reducing-power). To this end, the authors arranged the temperatures as abscissæ, and the reducing-powers as ordinates, of a curve, and found that, when acting on soluble starch, diastase showed the greatest activity at 50°, and the most favourable period at 50—55°. The ferment of ungerminated grain, on the other hand, showed the greatest activity at 50°, and the most favourable period at 45—50°. Moreover, at 4° the reducing-power of the grain ferment was as high as that of diastase at 14·5°; at 35° it was the same for both; but the maximum reducing-power reached by the grain ferment was 41·2, whilst that reached by the diastase was 51·0. It is thus seen that the grain ferment is less intense in its action at 50° than diastase is, but at the ordinary temperature the reverse is the case.

The following is a comparison of the above results for diastase with those of Kjeldahl, who used starch paste.

	Reducing power of diastase at		
	50°.	55°.	62°.
With soluble starch	50·16	50·02	27·30
,, starch paste	49·83	50·23	35·24

The authors doubt the existence of Reychler's artificial diastase (Abstr., 1889, 621); it is most probably identical with the ferment of ungerminated grain, and may possibly be this ferment and not a conversion-product of the gluten. The activity of diastase is not due to bacteria. A. G. B.

Synthesis of Alcohol-acids of the Pyridine Series. By A. EINHORN (*Ber.*, **23**, 219—224).—By the further investigation of ω-trichloro-α-hydroxypropylpyridine (Abstr., 1887, 845) a number of new pyridine-derivatives containing fatty residues have been obtained, some of which have an especial interest as standing in close relation to ecgonine and cocaïne.

Pyridyl-ω-trichloropropylene, $C_5NH_4\cdot CH\colon CH\cdot CCl_3$, is obtained by the action of phosphoric chloride on ω-trichloro-α-hydroxypropylpyridine. It crystallises from absolute alcohol in prismatic needles, melting at 97°.

Pyridyl-α-lactic acid, $C_5NH_4\cdot CH_2\cdot CH(OH)\cdot COOH$, is formed when an aqueous solution of ω-trichloro-α-hydroxypropylpyridine is boiled with sodium carbonate, and is isolated in the form of a basic copper salt, $(C_8H_8NO_3)_2Cu,CuO$. The free acid crystallises in transparent prisms which melt at 124—125°, and its *platinochloride* and *aurochloride* melt at 202—204° and 173—174° respectively. Its *methyl* salt, obtained by acting on the silver salt with methyl iodide, is a light-yellow oil, the aurochloride of which melts at 119°. The methyl salt does not yield a benzoyl compound directly, but it may be obtained by boiling the free pyridyl-α-lactic acid with benzoic anhydride, and treating the silver salt of the acid thus obtained with methyl iodide. It has the formula $C_5NH_4\cdot CH_2\cdot CH(OBz)\cdot COOMe$, and forms a light-coloured oil. Its *platinochloride* crystallises in light-yellow needles, which melt at 193° with decomposition.

Pyridylacrylic acid, $C_5NH_4\cdot CH\colon CH\cdot COOH$, is prepared by boiling ω-trichloro-α-hydroxypropylpyridine with alcoholic potash, pyridyl-α-lactic acid being formed at the same time. It is likewise formed when the latter is heated at 130—140° in a vacuum. It crystallises from hot water in stellate groups of white needles, which melt at 202—203°, and gives crystalline salts with the haloïd acids. The *aurochloride* forms pale yellow needles, melting at 194—195°, and the *platinochloride* reddish-yellow prisms, melting at 209—210°. Its salts with the alkali metals are gelatinous, but the calcium and silver salts are crystalline, and its methyl and ethyl salts likewise crystallise at low temperatures. It unites with methyl iodide, forming a methiodide, which crystallises from alcohol in needle-shaped crystals melting at 219—220°. Pyridylacrylic acid unites with bromine in acetic acid solution, forming a *perbromide*, but yields the *dibromide* at 100°; this crystallises from water in yellowish prisms melting at 127°.

Pyridyl-β-lactic acid, $C_5NH_4\cdot CH(OH)\cdot CH_2\cdot COOH$. When pyridylacrylic acid is heated at 100° with an acetic acid solution of hydrogen bromide in a sealed tube, it forms pyridyl-β-bromopropionic acid, $C_5NH_4\cdot CHBr\cdot CH_2\cdot COOH$, which crystallises in white needles, melting at 163—164°. If this be neutralised with a solution of sodium carbonate, and the liquid warmed, pyridylethylene or vinylpyridine, $C_5NH_4\cdot CH\colon CH_2$, is evolved, whilst pyridyl-β-lactic acid and regenerated pyridylacrylic acid remain in solution. The former is extremely soluble in water, and crystallises from it in slender, white needles. Its most characteristic salt is the *basic copper salt*, which forms well-developed sapphire-blue crystals. Its *hydrochloride* forms

compact prisms, melting at 145—146°, whilst the *platinochloride* melts at 191°. The *methyl* salt, prepared by passing hydrogen chloride into an alcoholic solution of the acid, is a pale yellow oil. The benzoyl compound of the methyl salt could not be obtained directly, but was prepared in the following manner. Ethyl pyridyl-β-lactate (or its hydrochloride) was boiled with benzoic chloride on the water-bath, poured into water, made alkaline with sodium carbonate, and extracted with ether. The oil remaining after the evaporation of the ether was dissolved in hydrochloric acid, and allowed to remain for a few days. The product is the hydrochloride of *benzoylpyridyl-β-lactic acid*, which decomposes on the addition of water, yielding the free acid. This crystallises from water in brilliant prisms, melting at 135·5°, and is converted into the *methyl* salt by heating its silver salt with methyl iodide in a sealed tube; this crystallises from ether in transparent prisms melting at 79°.

Pyridylglyceric acid, $C_5NH_4{\cdot}CH(OH){\cdot}CH(OH){\cdot}COOH$, is obtained by the careful oxidation of pyridylacrylic acid with dilute potassium permanganate. Its *hydrochloride* crystallises with 1 mol. of water, and melts at 189—190°. Its *ethyl* salt forms transparent tablets melting at 95—96°, and yields with benzoic chloride a crystalline compound which melts at 121—122°. H. G. C.

2′-Bromoquinoline. By A. Claus and G. Pollitz (*J. pr. Chem.* [2], **41**, 41—48).—2′-*Bromoquinoline* is obtained by heating carbostyril (1 part) with phosphorus pentabromide (3 parts) in a stream of dry carbonic anhydride at 120—130°, and distilling the product with steam; it crystallises from alcohol in lustrous, colourless needles, melting at 48—49° (uncorr.), and soluble except in water, which decomposes them on boiling. The *platinochloride* (with 2 mols. H_2O), the *methiodide*, and the *methochloride* and its *platinochloride* are described.

Three *nitro*-1′-*bromoquinolines* were obtained by nitrating 1′-bromoquinoline in the cold. (1) small, white needles melting at 244° (uncorr.); (2) lustrous prisms or tables melting at 146° (uncorr.), and distilling without decomposition at 225—228°; (3) yellow leaflets and needles melting at 111° (uncorr.). When these nitro-derivatives are boiled with water, they are converted into corresponding *nitrocarbostyrils* (compare Friedländer and Lazarus, Abstr., 1885, 1139), whose properties are as follows, taking the same order as above: (1) snow-white needles melting at 283° (uncorr.), and subliming; its *potassium salt* forms yellow needles; (2) yellow, strongly refractive, four-sided prisms melting at 163° (uncorr.), and sparingly soluble; its *potassium* and *sodium salts*, its *hydrochloride* (m. p. 159—160°) and its *platinochloride* are described; (3) small, yellow needles which melt at 302° (uncorr.), with decomposition and blackening; its *potassium salt* is described.

Only one sulphonic acid has as yet been obtained by sulphonating 1′-bromoquinoline (1 part) with 40 per cent. anhydrosulphuric acid (10 parts) at 120—130°. 1′-*bromoquinolinesulphonic acid* crystallises in small, colourless needles which melt with decomposition at 288—290°, but begin to darken in a capillary tube at 190°. The

potassium salt (with 2 mols. H_2O), the *barium salt* (with $2\frac{1}{2}$ mols. H_2O), the *copper salt*, the *silver salt* (with 1 mol. H_2O), the *methyl salt* (m. p. 190°), and the *ethyl salt* (m. p. 135° uncorr.) are described.

A *tribromoquinoline* is obtained by brominating the above sulphonic acid; it crystallises in long, lustrous, colourless, efflorescent needles, with 1 mol. H_2O, melting at 247—248° (uncorr., compare this vol., p. 267) to a brown oil, which solidifies again, and sublimes in slender, felted needles. A. G. B.

1 : 4-Hydroxyquinolinesulphonic Acid. By A. CLAUS and M. POSSELT (*J. pr. Chem.* [2], **41**, 32—41; compare this vol., pp. 265, 268).

1 : 4-*Hydroxyquinolinesulphonic acid*, prepared by the action of cold fuming sulphuric acid (6—8 parts) on 1-hydroxyquinoline (1 part), crystallises in long, colourless needles, containing 1 mol. H_2O, which is lost at 120°; it decomposes at about 270° without melting, and is soluble in alcohol, glacial acetic acid, and dilute hydrochloric acid; with diazo-compounds it gives red dyes, with ferric chloride a green colour, and with ferrous sulphate a dark-brown precipitate. The *normal sodium salt*, $OH{\cdot}C_9NH_5{\cdot}SO_3Na + H_2O$, the *basic sodium salt*, $ONa{\cdot}C_9NH_5{\cdot}SO_3Na + 2H_2O$, the *normal potassium salt* (with 1 mol. H_2O), the *basic potassium salt* (with 3 mols. H_2O), the *normal barium salt* (with 1 mol. H_2O), the *normal calcium salt* (with 1 mol. H_2O), and the *silver salt* are described. When this sulphonic acid is heated with methyl iodide in hydrochloric acid at 110°, *methylhydroxysulphone-betaïne* [SO_3 : OH : Me = 1 : 4 : 1′] is obtained as slender needles which decompose without melting at 250°.

Bromo-1 : 4-*hydroxyquinolinesulphonic acid* results from the action of bromine on the sulphonic acid (equal mols.), when they are gradually mixed; it crystallises in small prisms or needles which contain 1 mol. H_2O (lost at 120°), decomposes without melting at 280°, and is freely soluble in alcohol.

When bromine (2 mols.) is added (all at once) to the aqueous solution of the sulphonic acid (1 mol.), *dibromo*-1-*hydroxyquinoline* is obtained; it crystallises in lustrous, colourless needles, melting at 196° (uncorr.), and soluble in most solvents, except water and light petroleum.

The action of phosphorus pentabromide (2 mols.) on 1 : 4-hydroxyquinolinesulphonic acid at 130—140° produces *bromoquinolinesulphonic bromide*, $C_9NH_5Br{\cdot}SO_2Br$, which decomposes when heated with water, yielding 1 : 4-bromoquinolinesulphonic acid (Lellmann and Lange. Abstr., 1888, 296); this settles the constitution of 1 : 4-hydroxyquinolinesulphonic acid. If the hydroxyquinolinesulphonic acid (1 mol.) is heated with phosphorus pentabromide ($4\frac{1}{2}$ mols.) at 160—170°, a tribromoquinoline is produced, as well as the bromide; it melts at 168° (uncorr.; compare this vol., p. 173).

1 : 4-*Chloroquinolinesulphonic chloride*, obtained by the action of phosphorus pentachloride on 1 : 4-hydroxyquinolinesulphonic acid, forms small, colourless needles which decompose without melting.

1 : 4-*Chloroquinolinesulphonamide* crystallises in small, colourless needles, which have no melting point, and are insoluble in water, but soluble in other solvents.

1 : 4-*Chloroquinolinesulphonic acid* forms colourless needles with 1 mol. H_2O, decomposes without melting at about 280°, is sparingly soluble in water, and gives red dyes with diazo-compounds.

Trichloroquinoline forms slender, colourless needles, melting at 68°, (uncorr.).

1 : 4-*Dihydroxyquinoline*, obtained by fusing 1 : 4-hydroxyquinolinesulphonic acid with potash, crystallises in slender needles which are insoluble in water, and decompose without melting above 270°.

1-*Hydroxyquinolinedisulphonic acid*, obtained by heating 1-hydroxyquinoline with fuming sulphuric acid, forms large, colourless, prisms with 1 mol. H_2O, which is lost at 120°; it decomposes without melting about 280°.

A *dinitrohydroxyquinoline* has been obtained; it forms yellow needles which have no melting point.

The investigation of the above compounds is not yet complete.

A. G. B.

3-Hydroxyquinolinesulphonic Acid. By A. CLAUS and M. POSSELT (*J. pr. Chem.* [2], **41**, 158—160; compare Lippmann and Fleissner, this vol., p. 268).—3-*Hydroxyquinolinesulphonic acid*, obtained by sulphonating 3-hydroxyquinoline with fuming sulphuric acid, crystallises in yellow needles with ½ mol. H_2O; it decomposes at 270°, and dissolves sparingly in water, more freely in alcohol, but not in ether, chloroform, or benzene; it does not form dyes with diazo-compounds. The *neutral sodium* and *potassium salts* (each with 1 mol. H_2O) are described. With 1 mol. of bromine, the acid yields a *bromo-3-hydroxyquinolinesulphonic acid*, whilst with 2 mols. of bromine a *dibromo-3-hydroxyquinoline* crystallising in slender, yellow needles, soluble in alcohol and insoluble in water, is obtained. A. G. B.

The First Synthetically prepared Base Isomeric with Quinine. By C. A. KOHN (*J. Soc. Chem. Ind.*, **8**, 959—960).—With regard to Wallach and Otto's claim that pinolenitrol-β-naphthylamine (this vol., p. 170) is the first base isomeric with quinine that has been produced synthetically, the author points out that this is not the case, as three years back he synthesised hydroxyhydroethylenequinoline, an isomeride of quinine (Trans., 1886, 508).

Phen-α-phenylparazoxime. By E. LELLMANN and A. DONNER (*Ber.*, **23**, 172—174).—*Metanitrophenol phenacyl ether*,

$$NO_2 \cdot C_6H_4 \cdot O \cdot CH_2 \cdot COPh,$$

is best prepared by heating an intimate mixture of potassium orthonitrophenoxide and phenacyl bromide at 68° for 4 hours, the warm mass being triturated from time to time in order to ensure complete decomposition. The product is washed with water, then with dilute soda, and recrystallised from alcohol. It forms well-defined needles, melts at 118°, and is soluble in benzene, chloroform, and glacial acetic acid, but more sparingly in ether and alcohol, and almost insoluble in water and concentrated hydrochloric acid; it is decomposed by boiling soda, yielding orthonitrophenol.

Phen-α-phenylparazoxine, $C_6H_4<\begin{matrix}O\cdot CH_2\\ N:CPh\end{matrix}$, is obtained when the preceding compound is reduced with stannous chloride and concentrated hydrochloric acid; the intermediate product (amidophenol phenacyl ether) cannot be isolated. The acid solution is gradually poured into yellow ammonium sulphide, the precipitate washed first with ammonium sulphide and then with water, and recrystallised from warm alcohol. It forms colourless needles, melts at 102—103°, and is readily soluble in benzene, ether, chloroform, and mineral acids, but only sparingly in warm water, from which it separates in plates. When heated in small quantities, it distils with partial decomposition giving off a pleasant odour recalling that of oranges. It dissolves in concentrated hydrochloric acid and in sulphuric acid with a red coloration, which changes to yellow on adding water. The *platinochloride*, $(C_{14}H_{11}ON)_2,H_2PtCl_6$, and the *aurochloride* crystallise in microscopic plates and are unstable. Potassium dichromate and stannous chloride produce precipitates in solutions of the hydrochloride. F. S. K.

Preparation of Anhydro-bases from Amidomercaptans of the Fatty Series. By S. GABRIEL and P. HEYMANN (*Ber.*, 23, 157—160). *Phenylthiazoline*, $CPh\leqslant\begin{matrix}S\cdot CH_2\\ N\cdot CH_2\end{matrix}$, is obtained when thiobenzamide (20 grams) is boiled for about $1\frac{1}{2}$ hours with ethylene bromide (200 grams); after separating the unchanged bromide by distilling with steam, the solution is filtered, saturated with alkali, again distilled with steam, and the product (about 7 grams) extracted by shaking the distillate with ether. It is a yellowish oil with an odour of quinoline, and boils at 275—277° without decomposition. It dissolves freely in acids. The *picrate* crystallises from boiling water in long, yellow needles. The *platinochloride*, $(C_9H_9NS)_2,H_2PtCl_6$, is a yellow, crystalline compound. When a solution of the base in hydrochloric acid is treated with bromine, it is converted into a thick, brownish syrup (benzoyltaurine) which is readily soluble in water. This syrup gives benzoic acid and taurine when heated at 150—160° with concentrated hydrochloric acid; it also forms a crystalline silver salt of the composition $C_9H_{10}NSO_4Ag$. F. S. K.

Constitution of the Quinoxalines obtained from Toluylenediamine and Bromacetophenone. By E. LELLMANN and A. DONNER (*Ber.*, 23, 166—171).—*Phenacylparatoluidine*, $C_6H_4Me\cdot NH\cdot CH_2\cdot COPh$, is easily obtained by treating paratoluidine (2 mols.) with bromacetophenone (1 mol.) in cold alcoholic solution, and dissolving the product in hot concentrated hydrochloric acid, or recrystallising it from alcohol in order to separate the diphenacyl-derivative which is also produced. The *hydrochloride* and the *nitrate* crystallise in colourless needles. The free *base* crystallises from alcohol in large, yellow plates, melts at 134°, and decomposes when heated. It is readily soluble in benzene, more sparingly in alcohol, glacial acetic acid, and warm, concentrated hydrochloric acid, and it dissolves in concentrated sulphuric acid forming a colourless solution.

Diphenacylparatoluidine, $C_6H_4Me{\cdot}N(CH_2{\cdot}COPh)_2$, crystallises from xylene in colourless needles, melts at 255°, and is very sparingly soluble in alcohol, benzene, and concentrated hydrochloric acid; it is not decomposed by warm soda.

Phenacylmetanitroparatoluidine, $NO_2{\cdot}C_6H_3Me{\cdot}NH{\cdot}CH_2{\cdot}COPh$, is prepared by triturating phenacylparatoluidine with nitric acid of sp. gr. 1·138 (30 parts), and keeping the mixture for 48 hours. It crystallises from alcohol in golden needles, melts at 163—165° with decomposition, and is readily soluble in benzene and chloroform, but more sparingly in alcohol. This compound can also be obtained, but only in small quantities, by dissolving bromacetophenone and metanitroparatoluidine in alcohol, and keeping the solution for some time over anhydrous magnesia. The *dinitro*-compound, $C_{15}H_{13}O_5N_3$, obtained by dissolving phenacylparatoluidine in nitric acid of sp. gr. 1·4, crystallises in golden needles, melts at 156° with decomposition, and is readily soluble in benzene and chloroform, but only sparingly in alcohol; it is decomposed by warm soda.

When phenacylmetanitroparatoluidine is treated with stannous chloride and cold concentrated hydrochloric acid, it is converted into the corresponding amido-derivative; the latter is, however, unstable, and immediately decomposes into water and dihydrophenyltoluquinoxaline. This compound cannot be isolated, as it quickly undergoes oxidation on exposure to the air, being converted into phenyltoluquinoxaline (m. p. 79°), identical with one of the compounds obtained from toluylenediamine (compare Hinsberg, Abstr., 1887, 817). The constitution of this quinoxaline is, therefore, $C_6H_3Me{<}\begin{matrix}N{:}CPh\\ \vert\\ N{:}CH\end{matrix}$ [N : N : Me = 1 : 3 : 5], and that of the isomeride (m. p. 136°)

$$C_6H_3Me{<}\begin{matrix}N{:}CPh\\ \vert\\ N{\cdot}CH\end{matrix} \quad [N : N : Me = 1 : 3 : 4].$$

F. S. K.

Paradiazine-derivatives. By P. W. Abenius (*J. pr. Chem.* [2], **41**, 79—86; compare this vol., p. 268).—*Dioxanilide*,

$$NPh{<}\begin{matrix}CO{\cdot}CO\\ CO{\cdot}CO\end{matrix}{>}NPh,$$

is obtained by shaking together hot, glacial acetic acid solutions of diphenyldiketodihydroparadiazine (this vol., p. 268) and chromic acid; the anilide crystallises out after a time. It forms small, lustrous, thin, six-sided crystals (m. p. not given) sparingly soluble in the usual solvents; when heated with aniline it is converted into oxanilide. If a large excess of chromic acid is used, and the mixture heated for 15—20 minutes and then evaporated on the water bath, a residue of diphenylparabanic acid (Abstr., 1885, 1196) is left.

Dioxalparatoluidide, $C_6H_4Me{\cdot}N{:}(CO{\cdot}CO)_2{:}N{\cdot}C_6H_4Me$ [N : Me = 4 : 1], obtained in like manner to dioxanilide, crystallises in small, sparingly soluble, lustrous, six-sided leaflets melting above 300°. From the mother liquor, diparatolylparabanic acid (Abstr., 1878, 216) was obtained.

When diorthotolyldiketodihydroparadiazine is oxidised with chromic acid, only diorthotolylparabanic acid (Abstr., 1880, 244) is formed.

Diphenyldichlorodiketoparadiazine, $\begin{matrix} CO-CCl{\cdot}NPh \\ | \quad\quad | \quad\quad | \\ NPh{\cdot}CCl{\cdot}CO \end{matrix}$, produced by acting on diphenyldiketodihydroparadiazine with phosphorus pentachloride and oxychloride, decomposing with water, and dissolving the product in alcohol, crystallises in white needles or prisms (with 1 mol. alcohol), melting at 247°; by reduction it yields *diphenyldiketoparadiazine*, which is still under investigation.

Phenylorthotolyldichlorodiketoparadiazine,

$$\begin{matrix} CO-CCl{\cdot}N{\cdot}C_6H_4Me \\ | \quad\quad | \quad\quad | \\ NPh{\cdot}CCl{\cdot}CO \end{matrix} \quad [Me:N = 1:2],$$

obtained in the same way, crystallises in white needles melting at 174—175° and is soluble in alcohol, ether, and benzene.

Orthotolylparatolyldichlorodiketoparadiazine,

$$C_4N_2Cl_2O_2(C_6H_4Me)_2 \ [Me : N = 1 : 2 \text{ and } 1 : 4 \text{ respectively}],$$

crystallises in white, slender needles (with 1 mol. alcohol) melting at 146°.

A. G. B.

Derivatives of Aromatic Thiocarbamides. By D. S. Hector (*Ber.*, **23**, 357—370).—In a previous paper (Abstr., 1889, 872) the author has shown that phenylthiocarbamide is oxidised by hydrogen dioxide to *dianilido-orthodiazothiole*, $S{<}\begin{matrix} C(NHPh){:}N \\ | \\ C(NHPh){:}N \end{matrix}$. This name it is proposed to change to *diphenyldiamido-orthodiazothiole*, in accordance with Widman's nomenclature (*Journ. Prakt. Chem.*, **38**, 185). Further study has shown that this reaction is a general one for the aromatic mono- and di-substituted thiocarbamides. Only one of the latter has been prepared, namely, *tetraphenyldiimidotetrahydro-orthodiazothiole*, $S{<}\begin{matrix} C(NPh){\cdot}NPh \\ | \\ C(NPh){\cdot}NPh \end{matrix}$. This melts at 131°, and forms a hydrochloride and sulphate which are sparingly soluble in water, but readily in alcohol.

Di-α-naphthyldiamido-orthodiazothiole, $S{<}\begin{matrix} C(NH{\cdot}C_{10}H_7){:}N \\ | \\ C(NH{\cdot}C_{10}H_7){:}N \end{matrix}$. To prepare this compound, 2—3 grams of α-naphthylthiocarbamide are suspended in a litre of boiling water, and hydrochloric acid, and a solution of hydrogen peroxide are then added. After boiling for a short time, the separated sulphur is filtered off, ammonia added, and the precipitated di-α-naphthyldiamido-orthodiazothiole recrystallised from alcohol. It forms white needles which contain 1 mol. of alcohol; these readily assume a reddish tinge, and melt at 104°. When crystallised from acetone, it melts at 136°. It forms a light-brown double salt with mercuric chloride melting below 100°, and a similarly coloured *platinochloride*, $(C_{22}H_{16}N_4S)_2,H_2PtCl_6$, which melts with decomposition at 224—225°. The *silver nitrate*-derivative, $C_{22}H_{16}N_4S,AgNO_3$, is a white precipitate, insoluble in alcohol, which blackens in sunlight, whilst the *picrate*, $C_{22}H_{16}N_4S,C_6H_2(NO_2)_3{\cdot}OH$, crystallises with $\frac{1}{2}$ mol. of alcohol in yellow grains which melt under 100°. The *monacetyl*- and *monobenzoyl*-derivatives melt at 263° and 270° respectively.

Di-α-naphthyldiamido-orthodiazothiole cyanide, $\begin{array}{l} N-C\quad N(C_{10}H_7)\cdot C{:}NH \\ \vert \qquad \overset{\vert}{S} \qquad\qquad\quad \vert \\ N-\overset{\vert}{C}-N(C_{10}H_7)\cdot C{:}NH \end{array}$,

separates in a crystalline form when cyanogen is passed through a warm alcoholic solution of the base; it melts at 203°.

Di-β-naphthyldiamido-orthodiazothiole, $S\Big<\begin{array}{l} C(NH\cdot C_{10}H_7){:}N \\ C(NH\cdot C_{10}H_7){:}\overset{\vert}{N} \end{array}$, is predared by adding hydrogen dioxide to an alcoholic solution of β-naphthylthiocarbamide containing a little hydrochloric acid, filtering, and adding ammonia. It is thus obtained as a thick, white mass, which is very soluble in the ordinary solvents, but has not been obtained crystalline. It commences to melt at 100°, but is not completely melted below 110—117°. Its *hydrochloride* and *sulphate* are less soluble in water than the salts of the α-base, but dissolve more readily in alcohol. It also gives compounds with platinic chloride, mercuric chloride, silver nitrate, and picric acid, and yields *acetyl-* and *benzoyl-*derivatives melting at 203° and 247° respectively. *Di-β-naphthyldiamido-orthodiazothiole cyanide,* $C_{24}H_{16}N_6S$, crystallises from alcohol in indistinct prisms melting at 200°.

Diparatolyldiamido-orthodiazothiole, $S\Big<\begin{array}{l} C(NH\cdot C_7H_7){:}N \\ C(NH\cdot C_7H_7){:}\overset{\vert}{N} \end{array}$, is prepared from paratolylthiocarbamide and hydrogen dioxide. It crystallises from alcohol in thick, yellowish prisms which melt at 127°. Its hydrochloride crystallises from water in white needles which melt with decomposition at 233°. The salts and double salts are similar to those of the foregoing compounds; the *acetyl*-derivative melts at 166°, and the *benzoyl*-derivative at 186°. The *cyanide,* $C_{18}H_{16}N_6S$, crystallises from alcohol in thin plates, seemingly aggregates of slender needles, which melt at 190°.

Nitrosodiparatolyldiamido-orthodiazothiole, $S\Big<\begin{array}{l} C[N(NO)\cdot C_7H_7]\cdot C{:}N \\ C[NH \text{——} C_7H_7]\cdot C{:}\overset{\vert}{N} \end{array}$, is formed by the addition of potassium nitrite to a hydrochloric acid solution of the base. It forms a yellow precipitate with a greenish tinge, and melts at 247° with decomposition.

Diorthotolyldiamido-orthodiazothiole, $S\Big<\begin{array}{l} C(NH\cdot C_7H_7)\cdot C{:}N \\ C(NH\cdot C_7H_7)\cdot C{:}\overset{\vert}{N} \end{array}$, is obtained in a manner similar to the para-compound. It is very difficult to obtain crystalline, as it is very soluble in the ordinary solvents. It is thrown down from its solution in hydrochloric acid by ammonia as a white precipitate which melts at 135°. The same salts of this base have been prepared as of the foregoing, and also the *acetyl-* and *benzoyl-*derivatives, the first melting at 221°, and the second at 214°. The *cyanide,* $C_{18}H_{16}N_6S$, is not readily obtained crystalline, as it is also very soluble; it separates from its solution in alcohol and water in indistinct crystals which begin to melt at 89°. The *nitroso*-compound, $C_{16}H_5(NO)N_4S$, obtained in a manner similar to the corresponding paratolyl-compound, separates from alcohol in brown crystals which melt at 135°.

Dimetaxylyldiamido-orthodiazothiole, $S<\begin{matrix}C(NH\cdot C_8H_9)\cdot C{:}N \\ | \\ C(NH\cdot C_8H_9)\cdot C{:}N\end{matrix}$, is obtained in the same manner from metaxylylthiocarbamide; the latter compound is prepared from metaxylidine hydrochloride and ammonium thiocyanate, and forms a crystalline compound which is soluble in boiling water, more readily in alcohol, and melts at 176°. Dimetaxylyldiamido-orthodiazothiole is, like the foregoing tolyl base, difficult to obtain crystalline; it separates from its solution as an oil which after solidification melts at 79°. The *cyanide*, $C_{20}H_{20}N_6S$, melts at 103°, and the *nitroso*-derivative, $C_{18}H_{19}(NO)N_4S$, forms brown crystals which melt at 146°. H. G. C.

Narcotine. By W. Roser (*Annalen*, **254**, 334—358, 359—368; compare Abstr., 1888, 1115 and 1316, Abstr., 1889, 417).—In this paper, the author gives an account of experiments which have been made to ascertain the constitution of cotarnine.

Benzoylcotarnine, $C_{12}H_{14}NO_4Bz + \frac{1}{2}H_2O$, can be easily prepared by treating cotarnine with benzoic chloride and soda in the cold, according to Baumann's method. It crystallises from hot alcohol, in which it is very readily soluble, in long, colourless needles, melts at 122—123°, and is insoluble in water. The *oxime*,

$$NOH{:}CH\cdot C_8H_6O_3\cdot CH_2\cdot CH_2\cdot NMeBz,$$

separates from alcohol in small, colourless crystals, melts at 165—166°, and is readily soluble in alcohol and soda, but insoluble in water and ether. Benzoylcotarnine combines readily with phenylhydrazine, yielding a crystalline, unstable hydrazone.

Cotarnine oxime hydrochloride, $C_{12}H_{16}N_2O_4,HCl$, separates on cooling in small, yellowish needles when cotarnine is boiled for some hours with an alcoholic solution of hydroxylamine hydrochloride; it is readily soluble in water, but only moderately easily in alcohol. The crystalline *platinochloride*, $(C_{12}H_{16}N_2O_4)_2,H_2PtCl_6 + 2H_2O$, is sparingly soluble in cold, and is decomposed by boiling water. The *mercurochloride* crystallises from hot water in long, colourless needles. The free *oxime*, $C_{12}H_{15}NO_3{:}NOH$, prepared by decomposing an aqueous solution of the salt with sodium carbonate, crystallises from alcohol in short prisms, turns yellow at 150°, and melts at 165—168° with decomposition; it is insoluble in water, but moderately easily soluble in alcohol and alkalis.

Cotarnmethine methochloride, $C_{11}H_{11}O_4NMe_3Cl$, combines with hydroxylamine hydrochloride when warmed therewith for several hours in alcoholic solution, and on cooling, the hydrochloride of the nitrile, $C_{14}H_{19}N_2O_3Cl + 2\frac{1}{2}H_2O$, separates from the solution; the oxime could not be obtained. The *platinochloride* of the nitrile is crystalline and insoluble in water. The *mercurochloride* crystallises from hot water in needles. When the hydrochloride is warmed with soda, trimethylamine is evolved, and cotarnonenitrile separates from the solution in colourless needles.

Cotarnonenitrile, $CN\cdot C_8H_6O_3\cdot CH{:}CH_2$, crystallises from hot alcohol in long, colourless needles, melts at 160°, and is insoluble in water.

The *dibromide*, $CN\cdot C_8H_6O_3\cdot CHBr\cdot CH_2Br$, prepared by treating the nitrile with bromine in chloroform solution, crystallises from alcohol in yellowish prisms, melts at 140°, and is very readily soluble in chloroform.

Cotarnelactone, $\begin{matrix} CO-O \\ | \\ C_8H_6O_3 \end{matrix}\!\!>CH\cdot CH_2\cdot OH$, the intermediate product in the oxidation of cotarnone to cotarnic acid, is best prepared as follows: finely divided cotarnone (10 grams) is shaken with cold water (about 1 litre) and a 4 per cent. solution of potassium permanganate (10 grams) gradually added in small portions at a time, with constant shaking; if the process is carefully carried out, the cotarnone will have almost completely disappeared by the time the permanganate has been added, but if the addition takes place too quickly, the lactone in solution will be further oxidised, and some of the cotarnone will remain unchanged. The solution, which remains quite clear, is kept for some time to allow the manganese oxide to separate, then filtered, slightly acidified, and evaporated; on cooling, the lactone separates from the solution in small, shining crystals. The yield is about 9 grams. Cotarnelactone separates from alcohol in prismatic crystals, melts at 154°, and is only sparingly soluble in cold alcohol and water, but readily in the hot liquids. It separates unchanged from ammonia and from sodium carbonate solution, but it is decomposed by alkalis or alkaline earths, yielding a salt of cotarnelactonic acid.

Cotarnelactonic acid, $COOH\cdot C_8H_6O_3\cdot CH(OH)\cdot CH_2\cdot OH$, separates as an oil when hydrochloric acid is added to a concentrated solution of the lactone in soda, but on warming it is reconverted into the crystalline lactone. It is obtained in crystals when the lactone is boiled with water and the solution allowed to cool; it melts at about 90—100°, being reconverted into the lactone. The *barium* salt, $(C_{11}H_{11}O_7)_2Ba + 5H_2O$, prepared by boiling the lactone with baryta, crystallises in needles, and is partially decomposed by hot water.

Acetylcotarnelactone, $\begin{matrix} CO-O \\ | \\ C_8H_6O_3 \end{matrix}\!\!>CH\cdot CH_2\cdot OAc$, separates from glacial acetic acid in crystals, and melts at 174°; the *benzoyl*-derivative, $C_{18}H_{14}O_7$, crystallises from glacial acetic acid in plates, and melts at 184°.

Cotarnic acid is best prepared by dissolving cotarnelactone (1 part) and an alkali (2 parts) in water (50 parts), and gradually adding a 4 per cent. solution of potassium permanganate (= 2 mols. of oxygen) to the cold solution. The filtered solution is then acidified with acetic acid and concentrated; on cooling, or on rubbing, the potassium salt separates from the solution. 10 grams of the lactone yield 5 grams of the potassium salt.

Cotarnic acid does not yield methyl chloride when it is heated with hydrochloric acid, but the presence of one methoxy-group in the acid can be proved by Zeisel's method. When cotarnic acid is heated with hydriodic acid and amorphous phosphorus at 150—160°, it yields gallic acid. These decompositions, and the fact that cotarnic

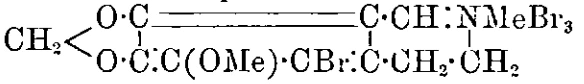
acid yields an anhydride, prove that it is a methylmethylenegallocarboxylic acid (methylmethylenetrihydroxyphthalic acid),

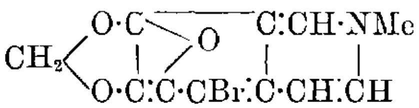
$$OMe\cdot C_6H(COOH)_2{<}{}^{O}_{O}{>}CH_2.$$

When cotarnic acid is warmed on the water-bath with hydrochloric acid, in sealed tubes, until the solution becomes greenish-yellow, it is decomposed into carbonic anhydride and methylmethylenegallic acid.

Methylmethylenegallic acid, $OMe\cdot C_6H_2(COOH){<}{}^{O}_{O}{>}CH_2$, crystallises from water and alcohol in needles, melts at 210° with previous softening, and is readily soluble in alcohol, but only sparingly in water. It dissolves in concentrated sulphuric acid with a yellow coloration, which on warming passes through green and becomes blue; the addition of water then causes the precipitation of a brown, flocculent substance. The *barium* salt, $(C_9H_7O_5)_2Ba$, crystallises in slender needles, and is readily soluble in hot, but only sparingly in cold water, and insoluble in alcohol. The *calcium* salt, $(C_9H_7O_5)_2Ca$, resembles the barium salt in crystalline form and in its behaviour with solvents.

Methylmethylenetribromopyrogallol, $OMe\cdot C_6Br_3{<}{}^{O}_{O}{>}CH_2$, is formed when cotarnic acid is treated with a slight excess of bromine in cold glacial acetic acid solution; on adding water, carbonic anhydride is evolved, and the bromo-derivative is precipitated. It crystallises from dilute alcohol in slender needles, melts at 160°, and is readily soluble in alcohol and ether, but insoluble in water and alkalis.

Constitution of Cotarnine.—It has previously been shown that cotarnine combines with acids with elimination of 1 mol. H_2O, yielding derivatives of isoquinoline. The compound previously described as bromocotarnine dibromide hydrobromide is readily converted into bromocotarnine hydrobromide by hydrogen sulphide, so that it is probably a perbromide; this perbromide, when heated, gives bromotarconine with elimination of methyl bromide (1 mol.) and hydrogen bromide (2 mols.). This reaction can be explained by assuming that bromocotarnine perbromide and bromotarconine have the constitution  and



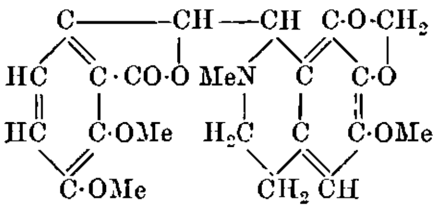
respectively. The above constitutional formula is in complete accordance with the properties of bromotarconine; a compound having this constitution would be a tertiary base, should give apophyllenic acid on oxidation, would be easily reduced, and its intense colour would be explained by the presence of the chromophore which characterises rosolic acid.

From these considerations, and from the experiments described above, it follows that cotarnine has the constitution

$$CH_2{<}^{O}_{O}{>}C_6H(OMe)(CHO)\cdot CH_2\cdot CH_2\cdot NHMe$$

[CHO : $CH_2\cdot CH_2\cdot NHMe$: H : OMe = 2 : 3 : 4 : 5].

Constitution of Narcotine.—In the narcotine molecule, $C_{22}H_{23}NO_7$, the hydrocotarnine- and opianic acid-groups are not combined together by any one of the seven oxygen-atoms, because of these five are combined with alkyls (three with methyl and two with methylene), and the other two are members of the lactone-group. Since, further, the five valency units of the nitrogen-atom are fully combined with carbon-atoms of the pyridine nucleus, the two groups cannot be united through nitrogen. It follows, therefore, that the hydrocotarnine- and opianic acid-groups are combined together by a carbon-atom of each and, without doubt, by those two carbon atoms which, on oxidation, are converted into the aldehyde-groups in opianic acid and cotarnine. Narcotine has, therefore, the constitution



It is a meconine-hydrocotarnine, and, like hydrastine, is nearly related to papaverine; both these opium alkaloïds are derivatives of a benzylisoquinoline. Hydroxynarcotine (this Journal, 1876, i, 461) is most probably an opianyl-hydrocotarnine, but narceïne, as has been shown by Claus and Meixner, is a naphthalene-derivative.

Methoxyhydrocotarnine methiodide, $C_{14}H_{20}NO_4I + \frac{1}{2}H_2O$, is formed when cotarnine, in cold methyl alcoholic solution, is treated with methyl iodide (1 mol.), and the solution kept for about three days; the methyl alcohol takes part in the formation of this compound, although cotarnine is not acted on by methyl alcohol alone. On evaporating, the product separates in yellow needles melting at 173° with decomposition. It loses its water at 120—130°, is readily soluble in hot water and alcohol, and dissolves unchanged in alkalis; it is therefore a quaternary ammonium iodide, but it differs from the isomeric compound (cotarnemethine methiodide) previously obtained (Abstr., 1889, 417) from cotarnine and methyl iodide. When treated with silver oxide, it gives a strongly alkaline base which is slowly decomposed by boiling water with liberation of dimethylamine. The *methochloride*, prepared by decomposing the methiodide with silver chloride, is hygroscopic, and gives an orange, crystalline, sparingly soluble *platinochloride* of the composition $(C_{14}H_{20}NO_4Cl)_2PtCl_4$. The base has the constitution $C_8H_6O_3{<}^{CH(OMe)}_{CH_2\cdot CH_2}{>}NMe_2I$.

Ethoxyhydrocotarnine methiodide, $C_{15}H_{22}NO_4I + \frac{1}{2}H_2O$, prepared by treating cotarnine with methyl iodide in ethyl alcoholic solution, as

described above, crystallises in small plates, melts at 168° with decomposition, and is more readily soluble in water and alcohol than the corresponding methoxy-derivative.

Isobutoxyhydrocotarnine methiodide, $C_{17}H_{26}NO_4I + H_2O$, separates in crystals when cotarnine is treated with methyl iodide in cold isobutyl alcoholic solution. It crystallises from hot water in needles or plates, and melts at about 120°.

Methyltarconic acid, $C_{11}H_{11}NO_3$, is obtained when steam is passed for a long time into a hot solution of tarconinemethyl hydroxide (1 part) in baryta (4 parts). After saturating with carbonic anhydride, the precipitate is warmed with dilute sulphuric acid, the filtered solution neutralised with sodium carbonate, concentrated, and the crystals obtained recrystallised from hot water. It crystallises in slender, yellow needles with 2 mols. H_2O, loses its water at 100°, melts at 244°, and is soluble in water, alkalis, and acids. It is isomeric with the compound (methyltarconic acid) previously obtained (Abstr., 1888, 1115) by boiling an aqueous solution of tarconinemethyl hydroxide; as the new compound is the true methyltarconic acid, the substance previously described must be called *pseudomethyltarconic acid*. The *hydrochloride*, $C_{11}H_{11}NO_3,HCl + H_2O$, crystallises in colourless needles or prisms, loses its water and turns yellow at 100°, and is moderately easily soluble in water and alcohol. The *sulphate* crystallises in small, colourless prisms, is readily soluble in water, and seems to contain water of crystallisation. The *platinochloride* is amorphous. F. S. K.

Hydrastine. By M. FREUND and A. ROSENBERG (*Ber.* **23**, 404—415).—Hydrastine unites with methyl iodide at 100°, forming *hydrastine methiodide*, $C_{21}H_{21}NO_6,MeI$, which crystallises in needles melting at 208° (compare Freund and Will, Abstr., 1887, 1057). By the action of silver chloride in aqueous solution it yields the corresponding *hydrastine methochloride*, $C_{21}H_{21}NO_6,MeCl$. When this compound is treated with a solution of potassium hydroxide, a yellow plastic mass separates; this will be described later. From the evaporated filtrate, white, lustrous prisms separate, which consist of *hydrastine methyl hydroxide*, $C_{21}H_{21}NO_6,MeOH + H_2O$; after recrystallisation from water or alcohol this compound melts at 242°. It was previously obtained by Freund and Will (*loc. cit.*) by acting on the methyl iodide with silver oxide. It may readily be reconverted into the chloride and iodide.

Methylhydrastine, $C_{22}H_{23}NO_6$, the above-mentioned yellow compound, is the chief product of the reaction, and crystallises from dilute alcohol in small, deep-yellow, needles melting at 156°. It is also formed when an alkali is carefully added to a hot aqueous solution of hydrastine methiodide. From its formation and analysis it must be regarded as methylhydrastine. It is almost insoluble in water, but dissolves in chloroform, benzene, and alcohol. With Frohde's reagent, it gives a violet coloration, which speedily becomes blue, and on standing changes to green, and finally becomes discoloured. Its salts, for the most part sparingly soluble, are even decomposed by ammonia and sodium carbonate; the *hydrochloride* melts at 241° with

decomposition, the *sulphate* at 250°, and the former yields double salts with stannous, zinc, and mercuric chlorides.

Methylhydrastine unites with methyl iodide very readily, forming *methylhydrastine methiodide*, $C_{22}H_{23}NO_6,MeI$, which crystallises in yellow needles, more soluble in hot water than in alcohol, and decomposing at 250°. It is readily decomposed by alkalis with evolution of trimethylamine and formation of a compound free from nitrogen which has the formula $C_{20}H_{20}O_8$.

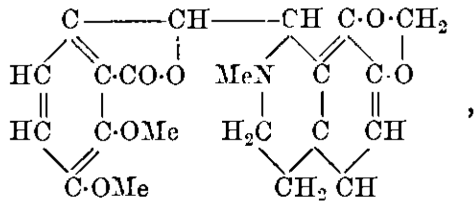
Methylhydrasteïne, $C_{22}H_{27}NO_8 + H_2O$. When an aqueous solution of hydrastine methochloride is warmed with an excess of potassium hydroxide, the precipitate first formed redissolves, and on neutralising the partially evaporated solution with acetic acid, colourless crystals of a substance having the above composition are obtained. It may also be more conveniently prepared by dissolving methylhydrastine in strong alkali, warming, and evaporating the solution until the oily mass becomes thick. The product is then dissolved in water, neutralised with acetic acid, and the substance recrystallised from water. It melts at 150—151°, is sparingly soluble in cold, more readily in hot water or alcohol, and loses its water of crystallisation at 100°. It shows both acid and basic properties, but is precipitated by carbonic anhydride from its alkaline solution. It forms salts with the strong acids, but not with acetic acid, and gives with Fröhde's reagent a colour reaction similar to that of methylhydrastine. It resembles in many respects the pseudonarceïne obtained by Roser (Abstr., 1888, 1316), which in the anhydrous state has the formula $C_{23}H_{27}NO_8$. An attempt to eliminate a second molecule of water from methylhydrasteïne, and obtain an anhydrous substance whose formula corresponded with that of pseudonarceïne, resulted only in the decomposition of the substance. Methylhydrasteïne is also a tertiary base, and readily unites with methyl iodide and is reconverted into methylhydrastine by warming with concentrated hydrobromic acid. Its salts are colourless, the *hydrochloride* forming spherical aggregates of crystals, melting at 290°.

Compounds similar to the above, containing the ethyl-group instead of methyl, have also been obtained. Hydrastine ethiodide and hydroxide, and ethylhydrastine have been previously obtained (Schmidt and Wilhelm, Abstr., 1888, 1212; Eykman, 1887, 505), and the authors have been able to confirm their results, with the exception of the melting points. This was found for hydrastine ethiodide to be 225° instead of 205—206°, and for ethylhydrastine 126—127° instead of 124°. The latter forms salts resembling those of methylhydrastine, and unites with ethyl iodide, forming *ethylhydrastine ethiodide*, $C_{25}H_{25}NO_6,EtI$, a beautifully crystalline substance which decomposes at 241°.

Ethylhydrasteïne is obtained in the same manner as the methyl-derivative, and crystallises from water in needles melting at 130°.

The above results make it evident that hydrastine is a tertiary base, and the formula given in the previous paper (Abstr., 1889, 1222), therefore requires modification. In a recent publication, Roser (preceding Abstr.) has proposed a formula for the closely allied alkaloïd narcotine, which shows at once its relation to papa-

verine and its lactone-like nature. The modified formula now proposed by the authors for hydrastine, viz. :—



corresponds well with Roser's narcotine formula. The formation of methylhydrastine, and the conversion of its methiodide into trimethylamine and a substance free from nitrogen can be readily explained, like the corresponding reactions of coneïne, by assuming that the piperidine ring is split (compare Ladenburg, *Ber.*, **14**, 2057). For methylhydrasteïne the following formula is regarded as the most probable :—

$$NMe_2\cdot C_2H_4\cdot C_6H_2(<^{O}_{O}>CH_2)\cdot CH(OH)\cdot CH(OH)\cdot C_6H_2(OMe)_2\cdot COOH.$$

H. G. C.

Hydrastine. By M. FREUND (*Ber.*, **23**, 416—417).—A personal discussion with E. Schmidt as to the priority of claim for the investigation of hydrastine. H. G. C.

Adenine and Hypoxanthine. By G. BRUHNS (*Ber.*, **23**, 225—229). —Adenine sometimes crystallises from slightly impure solutions in plates having a nacreous lustre, and differing entirely in appearance from the needles usually obtained. They have, however, the same composition and melting point.

When a solution of adenine hydrochloride is mixed with one of sodium picrate, adenine picrate is formed. This is very sparingly soluble in cold water (1 : 3500), more readily in alcohol and hot water, and crystallises from the latter in voluminous fascicular groups of yellow needles. It has the formula $C_5H_5N_5,C_6H_2(NO_2)_3\cdot OH + H_2O$, loses its water of crystallisation at 100°, and then remains unaltered at 220°. The author proposes to make use of this compound for the quantitative estimation of adenine, proceeding as follows :—Adenine and hypoxanthine are separated from xanthine and guanine in the usual manner by the addition of silver nitrate to the nitric acid solution. The mixture of adenine silver nitrate and hypoxanthine silver nitrate is then decomposed (the author obtains good results by employing for this purpose dilute hydrochloric acid in place of hydrogen sulphide), the resulting solution nearly neutralised with sodium carbonate. and a solution of sodium picrate added; after remaining 15 minutes, the precipitate is collected and washed. A correction of +2·2 milligrams must be made for each 100 c.c. of filtrate and wash water. The filtrate is then neutralised with ammonia, and the hypoxanthine precipitated with ammoniacal silver nitrate. No correction need be made for the solubility of hypoxanthine silver nitrate if there is no excess of ammonia in either solution.

Adenine and hypoxanthine combine, in aqueous solution, forming

a compound having the formula $C_5H_4N_4O,C_5H_5N_5 + 3H_2O$; this crystallises from water in aggregates of slender needles, which readily effloresce, and quickly lose water at 100°. It forms a homogeneous hydrochloride, but may be separated into its constituents by dissolving it in dilute sulphuric acid and submitting it to fractional crystallisation.

Adenine unites with dry bromine, forming a dark-red substance which appears to contain six atoms of bromine. It decomposes in the air, and more quickly at 100—120°, forming *bromadenine*, $C_5H_4N_5Br$, which crystallises in white stellate groups of needles insoluble in water, but readily soluble in ammonia, and is only attacked with difficulty by alcoholic potash. It is a strong base, and forms an insoluble picrate, which is more voluminous than that of adenine. A similar bromohypoxanthine could not be obtained.

H. G. C.

Ricin. By H. STILLMARK (*Chem. Centr.*, 1889, ii, 978—979; from *Pharm. Centralhalle*, **30**, 650—651).—The poisonous principle of the castor-oil bean is *ricin*, an albuminous substance which belongs to the group of unorganised ferments. It loses its poisonous properties at once if boiled, although it is not so severely affected by a dry heat. It is best separated by extracting the fresh castor-oil beans with a 10 per cent. sodium chloride solution, which extract, after filtration, is saturated with magnesium and sodium sulphates at the ordinary temperature. If this solution is cooled, the salts crystallise out, and with them a white precipitate which is readily separated by dialysis; this must be conducted at a low temperature or fermentation will ensue.

It would appear as though several members of the Euphorbiaceæ contain a poisonous albuminous substance, which may indeed be identical with that present in the castor-oil bean. The author draws attention to the fact that large quantities of the refuse of the castor-oil factories are allowed to remain in the open at the disposal of the public, and that since this substance is tasteless and more poisonous than arsenic, a considerable danger arises therefrom. J. W. L.

Action of Hot Water on different Albuminoïds. By S. GABRIEL (*Chem. Centr.*, 1889, ii, 988; from *J. Landw.*, **37**, 335—345).—Instigated by the results of his experiments on the action of superheated steam on the albuminoïds of lupins and rye, the author has conducted a series of determinations of the effect of water at comparatively high temperatures on albumin, fibrin, caseïn, conglutin, and wheat-gluten. The first result at which the author arrived is that if the same substance be heated with water under the same conditions, the same products in the same quantities are always obtained. The temperature would appear to exert a greater influence on the result than the time. Albumin, fibrin, and caseïn, for instance, when heated with water at 152° for six hours, were decomposed to the same extent as when heated at the same temperature for one hour; whereas when heated at 135° for three hours, the decomposition appeared not to proceed so far. Conglutin and wheat-gluten are more readily decomcomposed than the three first-named albuminoïds.

The following table gives the results of the action of water at 152° for six hours on the several albuminoïds :—

	Proteïn nitrogen.	Peptone nitrogen.	Amide nitrogen.
Albumin	37·04	25·90	37·87
Fibrin	36·97	29·88	33·15
Caseïn	35·09	27·86	37·05
Conglutin........	22·47	39·93	37·60
Wheat-gluten	26·45	59·28	14·28

J. W. L.

Physiological Chemistry.

Temperature in Nerves. By H. D. ROLLESTON (*J. Physiol.*, **11**, 208—225).—The observations were made by the help of an electrical resistance thermometer, invented by H. L. Callender, which is fully described. The conclusions arrived at are:—

(1.) During the passage of a nervous impulse there is no evidence of (even $\frac{1}{5000}$°) any heat being evolved from the nerve trunk.

(2.) In dying, a nerve does, however, evolve heat. In many cases sufficient heat is developed to raise the temperature of the thermometer in contact with it $\frac{1}{7}$°.

(3.) The development of heat roughly corresponds with the intensity of the natural nerve current; this, however, is not absolutely constant.

(4.) There is some evidence to show that nerves die at different rates.

W. D. H.

Artificial and Natural Digestions. By A. S. LEA (*J. Physiol.*, **11**, 226—263).—The following factors, present in normal digestion, are absent in artificial digestion experiments as usually performed in flasks and beakers:—(1) Constant movement of the contents; (2) constant removal of digestive products, (3) continuous additions of fresh portions of digestive fluid. In the present experiments, an apparatus was employed which tends to obviate these disadvantages. The artificial digestion is carried out not in a flask but in a tube of parchment paper, kept in constant up and down movement by connecting it to a motor; this tube is suspended in a cylindrical glass vessel, filled with the same mixture as that contained in the tube, but minus any ferment; an outer cylindrical glass vessel is filled with water kept at the necessary constant temperature. By this means, two of the more important conditions under which natural digestion takes place may be imitated, namely, continuous movement, and removal by dialysis of digestive products.

The first question investigated was the digestion of starch by saliva; the great contrast between natural and artificial digestion of

starch is the appearance of large quantities of dextrin in the latter case (opinions, however, differ as to the relative amounts of sugar and dextrin formed), whilst in the stomach and intestines mere traces of the dextrins are discoverable. Notwithstanding imperfections in the present method of experimentation, which are freely admitted, the contrast between a digestion carried on in the moving dialyser and in a flask is very marked; the iodine reaction of starch or dextrin disappears first in the contents of the dialyser; in prolonged digestions the contents of the dialyser remain clear and more free from putrefactive organisms than those of the flask, and the proportion of dextrin present is less in the dialyser than in the flask. This last point may be illustrated by the following table:—

	Duration of experiment in hours.	Strength of starch in solution per cent.	Dextrin per cent. in dialyser.	Maltose per cent. in dialyser.	Maltose per cent. in dialysate.	Dextrin per cent. in flask.	Maltose per cent. in flask.
1	6	0·4	7·67	—	—	15·23	—
2	22	2·4	8·58	—	—	14·16	84·23
3	21	4·23	16·78	—	—	36·62	61·81
4	68	4·23	8·48	—	—	35·70	62·33
5	18	0·43	10·31	12·42	76·67	—	—
6	48	4·18	12·61	14·20	71·15	—	—
7	90	3·35	4·29	3·06	91·18	—	—

The conclusions drawn from these and similar experiments are as follows:—

When the digestion of starch by saliva is carried out under conditions which ensure a very considerable removal of the products (maltose) as they are formed, then:—

1. The *rate* at which the digestion takes place is increased.

2. The total *amount* of starch converted into sugar is much greater, and the residue of dextrin is much less, than under conditions, otherwise similar, when the products are not removed.

3. The influence of the removal of digestion products on the relative amounts of dextrin and maltose formed is least marked when the starch solution is dilute.

4. These results justify the assumption that in the alimentary canal starch is completely converted into sugar before absorption.

5. The experiments afford no evidence that any sugar other than maltose is formed by the action of saliva on starch.

The next series of experiments dealt with the pancreatic digestion of proteïds; here the occurrence of an insoluble bye-product (antialbumid) is believed to be due to the imperfection of the method of artificial digestion, and probably does not occur in natural digestion; the question, however, which was specially investigated was the occurrence of leucine and tyrosine. Kühne has already stated that these amido-acids are formed in natural as well as in artificial pancreatic digestion, but careful quantitative experiments do not seem to have been made, although it may be roughly stated that less of these

materials are found in the intestine than in a flask. This may be due to one of two causes; either they are normally formed in large amount and then rapidly absorbed, or else they are formed in only small amount. By the help of the digesting dialyser, combined with the examination of the intestinal contents of animals, it was hoped in the present research to elucidate this question. A few typical experiments are described in detail and the following conclusions drawn:—(1) The undigested residue in a flask digestion is always greater than that of a dialyser digestion, other conditions being the same; (2) the amount of leucine and tyrosine formed in a flask digestion is always greater than in a dialyser digestion, other conditions being the same. The amount formed in a dialyser digestion is, however, always considerable, and it is possible that the amount formed is less than in a flask digestion, because the peptones from which they originate are continually dialysing out. Leucine and tyrosine were also found in not inconsiderable quantities in the intestines of the animals examined, not merely in microscopic amounts, as some previous observers seem to imply.

The paper concludes with remarks of a theoretical nature on the function of the amido-acids formed in plants and in animals. It is regarded as inconceivable that the animal, like the vegetable organism, should construct its proteïds from the nitrogen contained in the amido-acids, and their importance is likened to that of the inorganic salts and extractives contained in beef-tea, or other meat extract. We do not know what part these play exactly in the total processes of tissue-metabolism, but we do know that the salts are in some way essential, and that the extractives are an extremely important accessory to that metabolism.

Experiments on the pancreatic digestion of starch are in progress.

The term zymolysis is suggested as a convenient one to denote generally the changes produced by enzymes or unorganised ferments.

W. D. H.

The saving effect on Albumin of Organic Acids in Vegetable Foods. By H. WEISKE and E. FLECHSIG (*Bied. Centr.*, **19**, 31—39; from *Journ. f. Landw.*, **37**, 199—234).—The object of the experiments described in the paper was to determine whether the considerable quantities of organic acids which occur in sour fodder, and other foods in which fermentation occurs, have a physiological value similar to that of starch and some of the other non-nitrogenous food constituents. A rabbit was fed for some days on a mixture of meat meal (15 grams), fat (1·8 grams), starch (30 grams), sugar (10 grams), crude nut-shell fibre (5 grams), hay ash (0·5 gram), and salt (0·2 gram). The nutritive ratio was kept close, being as 1 : 3·7, in order that the action, if any, of the non-nitrogenous substances given might be more distinct. After eight days, the urine was collected for 10 days and the nitrogen determined. The average daily amount of nitrogen in the urine was 1·46 grams. The weight of the animal remained nearly constant (2390 grams). During the next period, a portion of the starch (10 grams) in the food was replaced by an equal amount of acetic acid, first as calcium, and afterwards as sodium acetate; but as after three days a considerable amount of food was left, lactic acid (10 grams), in

the form of calcium lactate, was substituted for the acetate. But this also had to be discontinued after three days. The live weight sank from 2345 to 2132 grams, and the average daily amount of nitrogen in the urine was 1·92 grams. So that, notwithstanding the less amount of nitrogen taken in the food, there was an increase in the amount eliminated. An amount of acetic or lactic acid as high as 4·3 grams per 1000 grams of live weight, therefore, not only does not save albumin, but it increases the albumin consumption. In the third period, in which the food used in the first period was again employed, the live weight attained nearly its original amount and the nitrogen of the urine again sank to 1·46 grams per day. In the fourth period, the same food-mixture was again used, but minus 10 grams of starch. In four days the live weight sank to 2225 grams, whilst the daily separation of nitrogen rose to 1·71 grams. Inasmuch as the amount of nitrogen separated during period II was still higher than this, it would seem that the presence of acetic or lactic acid in the food is actually prejudicial. In another experiment, in which only 2·2 grams of lactic acid per 1000 grams of live weight was used, there was no increased separation of nitrogen; but there was also no preservation of albumin.

The next experiments were made with a wether, fed for seven days with a mixture of meadow hay, starch, cane-sugar, earth-nut cake, and salt. The nutritive ratio was as 1 : 3·4. During the next period, lactic acid (60 grams) as calcium lactate was mixed with the food. It is shown that rather less proteïn, fat, and crude fibre were digested in the second period, and that the rise observed in the digested non-nitrogenous extract-substance was less than the lactic acid added. But there was more (1·73 grams) nitrogen deposited in the second period than in the first. There was thus a not inconsiderable deposition of albumin, caused by the presence of calcium lactate. With twice the amount of lactic acid, there was, however, an increased amount of nitrogen eliminated, whilst with still more acid the nitrogen of the urine was not raised, but there was a gradual rise in the amount of proteïn in the fæces.

Further experiments with a wether showed that the action of acetic acid (as sodium acetate) is quite different from that of lactic acid; the urine production was very much increased, and the urine was also somewhat richer in nitrogen. The undigested nitrogen of the fæces remained practically the same.

The results of the experiments do not support v. Wolff's view, that the volatile fatty acids (especially acetic acid) have a nutritive value but little less than that of the carbohydrates. N. H. M.

Amount of Substances yielding Oil of Mustard in various Foods, and their Action on the Animal Body. By ULBRICHT (*Bied. Centr.*, **18**, 53—56).—The seeds of black mustard contain two substances, potassium myronate and myrosin, which in presence of water react on each other, forming allylthiocarbimide and other compounds. The same or similar compounds are also obtained from the different organs of various species of *Allium*, and in small quantities from rape-seed. The author has determined the amount of mustard

oil which various seeds used in the oil factories of different countries will produce, as well as that of the seeds of weeds which accompany them. It has long been known that so-called rape cake, when treated with water, often develops a more or less powerful odour of mustard oil, owing to the adulteration of the cake with black or Indian mustard. Experiments, in which sheep had considerable amounts of black mustard mixed with their food, showed that a daily amount of 284 grams was not injurious, whilst a bull-calf consumed 148—444 grams with the same result. Cows took 343 to 820 grams of mustard a day, about a week before calving, without injury. Cake containing much potassium myronate may safely be given to quite young calves.

Although quite uninjurious to sheep and bullocks, it is doubtful whether, if given to cows, a cake containing potassium myronate may not have some influence on the taste and quality of the milk and butter; and it is suggested that, until more is known, cows should not be fed with oil cake which yields more than 0·5 per cent. of mustard oil. N. H. M.

Methyl Mercaptan as a Constituent of Human Intestinal Gases. By L. Nencki (*Monatsh.*, **10**, 862—863).—Planer and Ruge have shown that intestinal gas consists of carbonic anhydride, hydrogen, hydrogen sulphide, and marsh gas. Bearing in mind that methyl mercaptan is one of the products of putrifying albumin (compare Nencki and Sieber, this vol., p. 78), the author has endeavoured to show its presence as a degradation-product in human fæces, and that it is probably formed in the large intestine. To this end he reduced fresh excrement (3 kilos.) to a thin paste with water, added oxalic acid (90 grams), and distilled the mixture. The gases evolved, consisting in the main of carbonic anhydride, were first passed into a flask to condense the water, and then into a 3 per cent. solution of mercuric cyanide, which at first became yellow, and ultimately contained a small quantity of a black precipitate. This was collected, well washed, and treated with hydrochloric acid, the resulting gases being passed into a neutral solution of lead acetate, which assumed the characteristic odour of mercaptan, and ultimately contained a quantity of microscopic yellow plates or prisms insufficient for analysis. This unmistakable proof of the presence of mercaptan leads the author to suppose that alkaline compounds of mercaptan are decomposed in the large intestine by acids formed during the decomposition of albumins and carbohydrates; the liberated thio-alcohol being evolved in the gaseous form. G. T. M.

Uric Acid. By W. Roberts (*Proc. Med. Chir. Soc.*, 1890, 85—87).—The presence of uric acid in human urine is somewhat anomalous. As a vehicle for the elimination of nitrogen it is not needed; its place being taken by urea, which by its easy solubility is better adapted to the liquid urine of mammals. Perhaps uric acid is a vestigial remnant in mammalian descent; but although physiologically insignificant, uric acid is pathologically the most prominent component of the urine, this being chiefly due to its tendency to form concretions.

All acid urines tend inevitably to deposit their uric acid sooner or later. The time of onset of precipitation various from a few hours to five or six days, or even longer. The inference is drawn that pathological gravel is due to an exaggeration of conditions which exist in a less pronounced degree in health. To get at an explanation of this spontaneous precipitation, it is necessary to examine the states of combination of uric acid in urine.

Uric acid ($C_5H_4N_4O_3 = H_2\bar{U}$) is a bibasic acid, and forms two regular series of salts—namely, *normal urates* ($M_2\bar{U}$) and *acid* or *hydrogen urates* or *biurates* ($MH\bar{U}$). But in addition to these it forms a series of hyperacid combinations, first discovered by Bence Jones, and termed by him *quadrurates* ($MH\bar{U},H_2\bar{U}$). The normal urates are never found in the animal body, and are only known as laboratory products. The biurates are only encountered pathologically as gouty concretions. The quadrurates, on the other hand, are specially the physiological salts of uric acid. They constitute exclusively the combination in which uric acid exists in solution in normal urine, and they become visible sometimes as the amorphous urate sediment. The urinary excretion of birds and serpents is composed exclusively of quadrurates. The quadrurates can, moreover, be formed artificially under conditions which prevail in the animal body. The special and characteristic reaction of the quadrurates is that they are immediately decomposed by water into free uric acid and biurates.

They exist in acid urine in the presence of water and of superphosphates. These conditions necessarily involve the ultimate liberation and precipitation of uric acid. The first step is the breaking up of the quadrurate by the water of the urine into free uric acid and biurate according to the following equation:

$$\underset{\text{Quadrurate.}}{(MH\bar{U},H_2\bar{U})} + H_2O = \underset{\text{Free uric acid.}}{(H_2\bar{U})} + \underset{\text{Biurate.}}{(MH\bar{U})}.$$

This explains the liberation of half the uric acid. But the biurate thus formed is forthwith changed in the presence of superphosphates into quadrurate. Thus:

$$2\underset{\text{Biurate.}}{(MH\bar{U})} + \underset{\text{Superphosphate.}}{(MH_2PO_4)} = \underset{\text{Quadrurate.}}{(MH\bar{U},H_2\bar{U})} + \underset{\text{Dimetallic phosphate.}}{(M_2HPO_4)}.$$

By these alternating reactions all the uric acid is at length set free.

Seeing that uric acid exists in acid urine (that is, for some 16 hours out of the 24) amid conditions which, if the quadrurate stood alone and uncontrolled, would lead to its immediate precipitation, and yet that in the normal course no such early precipitation occurs, it is obvious that the urine must contain certain ingredients which inhibit or greatly retard the action of the water in breaking up the quadrurates. These inhibitory ingredients consist, chiefly, of (1) the mineral salts, (2) the pigments of the urine.

The conditions of the urine which tend to accelerate the precipitation of uric acid as in the formation of concretions and deposits, are —(1) high acidity, (2) poverty in mineral salts, (3) low pigmentation, (4) high percentage of uric acid. The converse conditions tend

to retard precipitation. On the interaction of these factors the occurrence or non-occurrence of uric acid gravel appears to depend, and probably the most important of these factors is the grade of acidity. W. D. H.

Physiological Action of Selenious Acid. By C. CHABRIÉ and L. LAPICQUE (*Compt. rend.*, **110**, 152—153).—0·2 per cent. of seleuions acid prevents the putrefaction of infusions of beef by the ordinary microbes of the air. With a smaller quantity, putrefaction takes place and the selenious acid is reduced.

Sodium selenite introduced into the blood of a dog, killed it when the dose reached 3 milligrams per kilo. of body weight. The most pronounced symptoms are intense congestion of all the viscera, and an abundant bronchial secretion of a rose-coloured liquid which contains no selenium.

Sodium selenite therefore acts essentially as an irritant, as Rabuteau observed, but the authors were unable to discover any of the crystals which he described as being present in all the organs. C. H. B.

Physiological Action of Sulphonal. By J. GORDON (*Brit. Med. J.*, i, 1890, 710—714).—From observations and experiments on the lower animals and on human beings, the following conclusions are drawn:—Sulphonal reduces the excitability of the reflex function of the spinal cord, and diminishes peripheral sensation. In men, large doses slow the respiration, but do not affect the pulse. It destroys slowly the conductivity of motor nerves, and the irritability of muscles, which subsequent washing with salt solution tends to revive. Urea is excreted in increased quantity after small doses (5—10 grains), in diminished quantity after larger doses; the volume of the urine is, however, not affected. It produces no effect on the skin, or on the body temperature; it, however, occasionally causes vomiting and diarrhœa. Although incoordination of the extremities, giddiness, and a feeling of depression or confusion sometimes follow its administration, as a rule these effects do not supervene, and the sleep which follows its use is tranquil and refreshing. The hypnotic action of the drug is marked even in healthy people, and in cases of insomnia it is found most trustworthy. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Decomposition of Albumin by the Bacillus of Malignant Œdema. By R. KERRY (*Monatsh.*, **10**, 864—873; compare Nencki, this vol., p. 78).—The author has investigated the decomposition of serum albumin by a pure culture of the bacillus of malignant œdema. On distillation, after saturation with oxalic acid, the fermented liquid gave gaseous products, and an oily liquid which when pure boils at 165—171°, has the formula $C_8H_{16}O_4$, and is of a ketonic

or of an aldehydic nature. It is optically active $[\alpha] = +5{\cdot}63$, and may, therefore, be assumed to contain an asymmetric carbon-atom; it gives a violet coloration with magenta decolorised with sulphurous acid, and a violet-red coloration with diazobenzenesulphonic acid, soda, and sodium amalgam. It reduces an ammoniacal solution of silver nitrate without the formation of a mirror, gives a crystalline compound with phenylhydrazine and sodium acetate; but does not react with sodium hydrogen sulphite or reduce Fehling's solution. On oxidation it is converted almost entirely into valeric acid. On evaporating the distillation residue and exhausting it with ether, leucine, hydroparacoumaric acid, and a small quantity of fatty acids, but no indole or scatole (compare Nencki, *loc. cit.*), were obtained. The gases produced in the fermentation consisted of carbonic anhydride, hydrogen sulphide, marsh-gas, and hydrogen in varying proportions. G. T. M.

Decomposition of Gelatin by Anaërobic Ferments. By L. SELITRENNY (*Monatsh.*, **10**, 908—917).—The author has used the method adopted by Nencki (this vol., p. 78) to investigate the decomposition of a solution of gelatin by *Bacillus liquefaciens magnus* and the *Rauschbrand bacillus*. With the former ferment, a considerable quantity of methyl mercaptan is formed during the progress of growth of the organism, the other products being volatile fatty acids, phenylpropionic acid, glycocine, leucine, and a considerable quantity of the so-called "*gelatin-peptone*," but no indole, scatole, or phenol is formed. When the fermentation is induced by the *Rauschbrand bacillus*, the same products together with phenylacetic acid are obtained, and in this case also the fermented liquid gives no indication of its containing indole, scatole, or phenol. On oxidising the gelatin-peptone with fuming nitric acid or with permanganate, succinic and benzoic acids are obtained.

From these results, the author infers that the benzoic acid, obtained by earlier observers on oxidation of gelatin, was derived from phenylpropionic acid, and that albumin and gelatin differ in that the latter on fermentation gives rise to a large quantity of glycocine, but to neither parahydroxyphenolpropionic acid, scatol acetic acid, nor to any of their derivatives. G. T. M.

Formation of Nitrates in Plants. By BERTHELOT (*Compt. rend.*, **110**, 109).—The facts observed by Heckel (next abstract) and by Lundström, combined with the results of André and those obtained by the author concerning the formation of nitrates by various species of *Amaranthus*, prove that there is a close connection between the life processes of the microbes in the soil and those which inhabit and develop in plants, whether they are microbes which fix nitrogen in vegetable soils and in legumes, or those which form nitrates in *Amaranthus*, *Sterculia*, the coffee plant, or vegetable soils.

C. H. B.

Utilisation and Transformations of Alkaloïds during the Germination of Seeds. By E. HECKEL (*Compt. rend.*, **110**, 88—90). —The seeds of *Sterculia acuminata* contained 2·37 per cent of caffeïne.

After the first year, the cotyledons, which remain attached to the stalk, contained only 1·072, after the second year 0·70, and after the third year 0·21. As the caffeïne disappears, chlorophyll and potassium nitrate are formed in the cotyledon, and hence its disappearance is due to a kind of nitrification.

In order to investigate the behaviour of pyridic alkaloïds, seeds of *Strychnos nux vomica* and *Datura stramonium* were used. After two to three months, according to the size of the seeds, all the alkaloïds had disappeared and been converted into more assimilable products, the change taking place under the influence of the embryon, for if the germs are removed from the seeds, the latter remain unaltered in moist earth for a long time.

In *Physostigma venenosa* the eserine undergoes transformation in the cotyledons themselves during the germinative movements, for whether the seeds are sown with or without their gemmule the eserine disappears, and it follows that the cotyledons contain substances which produce this change.

Whether the seeds have an endosperm or not, the disappearance of the alkaloïds becomes complete, and they pass into the young plant. The exact changes which they undergo are not yet known, but they are undoubtedly true reserves of food for the young plants, which, however, must undergo complete alteration before they can be assimilated. Reveil's observations that plants watered with solutions of their own alkaloïds always died, show that they cannot be absorbed directly with impunity. C. H. B.

Sugar-yielding Insoluble Carbohydrates in Seeds. By W. Maxwell (*Amer. Chem. J.*, 12, 51—60).—The finely-ground seeds were extracted with ether, to remove fats, and with dilute aqueous potash, to remove proteïds, and the residue was washed with water until neutral, and treated with a solution of diastase to separate the amyloïds. The insoluble residue, consisting of cellulose, remnants of less soluble albuminous matters, and "nitrogen-free extractive matter," was boiled for one hour with a 3·5 per cent. solution of sulphuric acid; the filtered extract was boiled for two hours in a reflux apparatus, and then neutralised with barium carbonate. The neutral solution was evaporated to a syrupy consistence, and extracted with alcohol. The alcoholic extract was evaporated, and the action of the residue on Fehling's solution and on polarised light was studied, as well as the products which it yielded when oxidised with nitric acid. It is found that the insoluble non-nitrogenous matters, exclusive of cellulose, are carbohydrate substances which, when treated with a dilute mineral acid, are convertible into sugars. This sugar is generally galactose; hence the carbohydrate is in most cases paragalactin; occasionally some levulose appears to be also obtained. The seeds of *Pisum sativum* and *Phaseolus vulgaris* contain respectively about 20 and 10 per cent. of insoluble carbohydrates, and this is all convertible into galactose. *Faba vulgaris* and *Vicia sativa* contain respectively 14 and 15 per cent. of insoluble carbohydrates, and not more than half of these can be converted into sugars by the action of a dilute mineral acid.

These insoluble carbohydrates are secreted in the cells of the endosperm. It is found that the thick membranes of the cells of the cotyledons are insensible to colour reagents, and do not dissolve in a cuprammonic solution, but after they have been boiled with dilute acid, and the carbohydrates thereby removed, the residue gives all the cellulose reactions. C. F. B.

Constituents of Urtica urens, Urtica dioïca, and Urtica pilulifera. By L. REUTER (*Chem. Centr.*, 1889, ii, 991—992, from *Pharm. Centralhalle*, **30**, 609—610).—From the leaves of these plants no alkaloïd could be separated, but by treatment with slaked lime, a glucoside is obtained; this reduces Fehling's solution very slightly; but after boiling with acids it reduces it readily. The product of boiling with acids is a brown, tarry substance. The glucoside contains no nitrogen. Tannin and salt do not precipitate it. Iodine in potassium iodide solution and potassiomercuric iodide form precipitates; potassium ferricyanide and potassium chromate in sulphuric acid are reduced by it. Its aqueons solution has a neutral reaction.

From the seeds of *Urtica pilulifera*, a green, fatty oil, containing chlorophyll, is obtained by treating them with magnesia and water, drying, and extracting with chloroform; the extract contained neither glucoside nor alkaloïd. The seeds, after treatment with chloroform, yielded a glucoside soluble in absolute alcohol. J. W. L.

Influence of Gypsum and of Clay on the Conservation of Soil Nitrogen, on Fixation of Atmospheric Nitrogen, and on Nitrification. By PICHARD (*Ann. Agronom.*, **15**, 505—521).—The author has made a number of experiments on the nitrification of the nitrogen of arachida cake when mixed with artificial soils composed of pure silicious sand of different degrees of fineness, mixed with varying proportions of gypsum, clay, and common salt. The mixtures were seeded with the washings of arable soil, and the initial and final nitrogen in the forms of ammonia, nitrates, and total nitrogen were estimated; the following conclusions were arrived at. In mixtures containing 1 per 1,000 of cake with the nearly pure sands, kept very slightly moist, and without vegetation for 18 months, the loss of nitrogen (greatest in the coarse sand) was as much as 70 per cent., and less than 15 per cent. was found as nitrate or ammonia at the end of that time. The addition of 5 per 1,000 of gypsum reduced the loss of nitrogen to 58 per cent. at most, the difference being due to more nitrogen nitrified. Salt in the proportion of 1 per 1,000 does not at all interfere with this beneficial action of gypsum. The addition of 10 per cent. of pure clay to the sand reduces the loss of nitrogen, and more is found as ammonia. One part per 1,000 of gypsum, in mixtures containing from 10 to 40 per cent. of clay, reduced still more, and progressively, the loss of nitrogen. One of these mixtures (that with 40 per cent. clay), containing 0·1023 per cent. initial nitrogen, showed a gain over the 18 months of 0·0293 per cent., equal to 28·53 per cent. of the initial nitrogen; the author regards the greater part of this gain as consisting of free nitrogen fixed from the air. J. M. H. M.

Preparation of Silage. By O. KELLNER and J. SOWANO (*Landw. Versuchs-Stat.*, 1890, 16—22).—In continuation of his former researches made with the object of determining the form in which nitrogen is lost during the preparation of silage, the author ensiled some *Lespedeza cyrtobotyra, Miq.*; and after a certain time had elapsed, a portion was extracted with cold water, and the solution distilled; in the distillate were found ammonia, and a small quantity of what appeared to be a substituted ammonia. It was also noted that the upper layers in the silo contained less nitrogen than the lower. The loss of nitrogen as ammonia in silage made from green maize was small. The author criticises the work of other workers on the same subject.

E. W. P.

Digestibility of Rice-Straw. By O. KELLNER (*Landw. Versuchs-Stat.*, **37**, 23—26).—Sheep were fed for a time on irrigated rice-straw and for another period on upland rice-straw (rice cultivated on dry lands); in both cases the live weight remained practically constant. The following table shows the composition of the straws, and their mean coefficients of digestion:—

	Paddy straw.	Coefficient of digestibility.	Upland rice.	Coefficient of digestibility.
Moisture on the dry ...	20·79	—	10·33	—
Albumin..............	6·80	46·54	6·75	43·84
Fat	2·17	41·45	2·16	51·90
Fibre..................	48·68	58·10	40·35	55·24
Non-nitrogenous extract.	24·80	35·41	32·14	28·86
Ash	17·55	—	18·60	—
Dry matter............	—	43·86	—	39·18
Organic matter	—	49·88	—	44·03

Both of these straws surpass all other straws as fodder.

E. W. P.

Analytical Chemistry.

New Form of Air-Bath. By M. A. ADAMS (*Analyst*, 1889, 222—228).—The apparatus consists of an outer jacket, within which is a copper vessel containing an annular thermostat. This is composed of two concentric cylinders of sheet copper, joined at the top and bottom, and enclosing an air space 5 mm. thick. This thermostat forms the wall of the drying chamber. It is connected with a U-tube, containing mercury for the control of the gas as usual. Air admitted at the bottom, between the jacket and the copper

vessel, rises to the top, and there enters the space between the walls of the vessel and the thermostat, by which it is deflected downwards to enter the drying chamber through a perforated shelf at the bottom. Access to the drying chamber is obtained by removing a dome-shaped glass chimney. The drying chamber is about 9 inches high and 12 in diameter, and the whole space above 4 inches from the shelf has a uniform temperature, whilst 7 cubic feet of air pass through it per minute. M. J. S.

Detection of Free Chlorine in Hydrochloric Acid. By G. A. Le Roy (*Bull. Soc. Chim.* [3], **2**, 729; compare this vol., p. 289).—When a few crystals of diphenylamine are added to hydrochloric acid containing traces of chlorine, a blue coloration is produced the intensity of which varies with the amount of free chlorine present. T. G. N.

Detection of Sodium in Lithium Carbonate. By W. H. Symons (*Chemist and Druggist*, **36**, 153, 291).—Since lithium chloride is readily soluble, whilst sodium chloride is only sparingly soluble (1 in 450—500) in concentrated hydrochloric acid, the treatment of a mixture of the two carbonates with about 10 parts of strong acid will reveal the presence of 2 or 3 per cent. of the sodium salt by the formation of a crystalline precipitate. For a quantitative separation, the acid should be previously saturated with sodium chloride, and a filter toughened by nitric acid (Francis) should be used. One part of lithium carbonate requires for solution 68·9 parts of water at 15°; the sodium carbonate can therefore be washed out, and tested for by hydrochloric acid in the residue of the evaporated washings. M. J. S.

Estimation of Copper by Titration with Potassium Cyanide. By G. E. R. Ellis (*J. Soc. Chem. Ind.*, **8**, 686—687).—Referring to the interference caused by the presence of zinc and iron in estimating the percentage of copper by titration with potassium cyanide, the author finds that the presence of 4 to 5 per cent. of zinc does not practically affect the correctness of the indications afforded by the potassium cyanide solution, but that when the zinc exceeds that amount, the indications are perfectly untrustworthy, necessitating the removal of the zinc before titration is effected. With regard to iron, the author's investigations are not yet complete. The present results show that the percentage of copper found is always low when a considerable amount of iron is present, owing probably to the retention by the precipitated hydroxide of a portion of the blue ammoniacal compound. D. B.

Precipitation of Copper as Thiocyanate in Assaying. By F. Johnson (*J. Soc. Chem. Ind.*, **8**, 603—604).—The ore is dissolved in any suitable acid, the excess being in great part boiled off. The moist residue is now diluted with about 20 times its volume of water, and ammonium thiocyanate added to the extent of at least three times the weight of copper possibly present. Stannous chloride solution is then added until bleaching of the deep-red coloured liquid ensues

and a solution more or less turbid from precipitated cuprous thiocyanate and the insoluble portion of the ore is obtained; this is passed through a filter and washed once with water containing about 1 per cent. of hydrochloric acid. The filter-paper, with its contents, is then transferred to the dissolving flask, treated with 50 c.c. of a dilute acid mixture of 1 part of nitric acid, 1 of hydrochloric acid, and 4 of water, and boiled gently for about a quarter of an hour. Ammonia is now added and the solution titrated with standard potassium cyanide. D. B.

Estimation of Minute Quantities of Aluminium in Iron and Steel. By J. E. STEAD (*J. Soc. Chem. Ind.*, **8**, 965—966).—Dissolve 11 grams of the iron in 44 c.c. of strong hydrochloric acid (or 22 grams in 88 c.c. if less than 0·01 per cent. of aluminium is expected) on the sand-bath in a 600 c.c. beaker. Evaporate to dryness, redissolve in hydrochloric acid and water, filter into a 500 c.c. beaker, and wash. The total bulk should not exceed 200 c.c. Add 3 c.c. of a saturated solution of sodium phosphate, then dilute ammonia until the free acid is neutralised. Now add hydrochloric acid, drop by drop, until the solution is clear, heat to boiling, add a large excess of a saturated solution of pure sodium thiosulphate (50 c.c. is sufficient), and continue to boil for about one hour. The precipitate is then collected on a filter, washed, treated with 5 c.c. of hydrochloric acid and 5 c.c. of boiling water, and the filtrate evaporated to dryness in a platinum dish. The residue from the evaporation is now fused with 2 grams of pure sodium hydroxide (dissolved in 1 c c. of water), after which it is cooled and dissolved in boiling water, the solution being made up to 110 c.c. The insoluble oxides are then filtered off, 100 c.c. of the filtrate (= 10 grams of iron) is neutralised with hydrochloric acid, and treated with 3 c.c. of sodium phosphate and a large excess of sodium thiosulphate. The mixture after boiling is treated with 2 c.c. of ammonium acetate and boiled for five minutes longer. The precipitate is collected, washed with hot water, ignited, and weighed. It consists of $AlPO_4$, and therefore contains 22·36 per cent. of aluminium. D. B.

Convenient Solution for Use in Titrating Weldon Muds for Manganese Peroxide. By W. G. M'KELLAR (*J. Soc. Chem. Ind.*, **8**, 968—969).—The author recommends the use of standard solutions of potassium dichromate and ferrous sulphate containing 11·862 grams and 69·4 grams per litre respectively. 1 c.c. = 0·04 pound of MnO_2 per cubic foot when using 1 cubic inch of the mud.

D. B.

Assay of Emetine in Ipecacuanha Wine. By T. P. BLUNT (*Pharm. J. Trans.* [3], **20**, 380).—The method recently described (this vol., p. 310) having been adversely criticised, the author has made further investigations, and finds the process is useless.

General and Physical Chemistry.

Production of Monochromatic Light. By E. FLEISCHL V. MARXOW (*Ann. Phys. Chem.* [2], **38**, 675—676).—The author recommends the use of sodium bromide in place of the chloride for the production of monochromatic light, as the former melts without decrepitation, and gives a much brighter light than the latter.

H. C.

Refractive Indices of Normal Salt Solutions. By C. BENDER (*Ann. Phys. Chem.* [2], **39**, 89—96).—The author showed (Abstr., 1884, 144) that Valson's law of moduli could be extended so as to represent the specific gravity of aqueous salt solutions as an arbitrary standard plus the product of the molecular concentration into the sum of two constants, one determined by the metal of the salt, and the other by the salt-radicle. From an investigation of aqueous solutions of the chlorides, bromides, and iodides of sodium, potassium, and cadmium, he now finds that the same mode of expression holds good for the refractive index (compare Walter, this vol., p. 202).

J. W.

Molecular Refraction of the Halogen Salts of Lithium, Sodium, and Potassium. By R. WEGNER (*Chem. Centr.*, 1890, i, 78—79).—The author has determined the molecular refraction of the chlorides, bromides, and iodides of potassium, sodium, and lithium, the index of refraction of the pure salts being first of all determined, and the molecular refraction being then calculated by means of Landolt's formulæ $M = P\frac{n-1}{d}$ and $M = P\frac{n^2-1}{(n^2+2)d}$, in which $P =$ the molecular weight, $n =$ index of refraction, $d =$ specific gravity. Difficulties were encountered first of all with the determination of the index of refraction of the pure salts from that of their solutions, the index increasing slightly as the concentration decreased, so that only an approximate result could be arrived at. The molecular refraction of the several salts calculated from the aqueous solutions varies slightly, therefore, with the concentration. If it be accepted that the atomic refraction of the several halogens does not vary in their different salts, then that of the alkali metals increases considerably with the atomic weight of the halogen with which it may be combined. The author regards it, however, as probable that the atomic refractions of the elements are not constant in compounds, but that they influence each other.

J. W. L.

Electrical Resistance of Iron and its Alloys at High Temperatures. By H. LE CHATELIER (*Compt. rend.*, **110**, 283—286). —The resistance is expressed in ohms per mm. of wire 1 mm. in diameter.

Pure soft iron—carbon 0·05 per cent.—

t. ...	15°	290°.	460°.	750°.	800°.	860°.	910°.	1060°.
R ...	0·14	0·38	0·59	1·10	1·21	1·31	1·34	1·40

Cast steel, medium hardness—carbon 0·6, manganese 0·4 per cent.—

t. ...	15°.	300°.	420°.	600°.	700°.	820°.	960°.	1100°.
R ...	0·16	0·43	0·55	0·80	0·97	1·28	1·32	1·34

Hard steel—

t. ...	15°.	280°.	410°.	680°.	730°.	830°.	870°.	940°.	1050°.
R ...	0·24	0·46	0·60	1·06	1·13	1·39	1·43	1·46	1·48

The angular points in the curves representing the variations in the electrical resistance of iron and steel, show clearly the two alterations of state described by Osmond (see this vol., pp. 566, 567), and also that the temperature at which the changes take place is independent of the proportion of foreign matter present.

An alloy of iron with manganese, containing 13 per cent. of the latter, shows only one indefinite angular point at abont 700°. Nickeliferous iron shows a very distiuct angular point at 340°.

The variation in the electrical resistance of platinum and of a platinum-rhodium alloy is proportional to the temperature.

When an alloy of iron with 25 per cent. of nickel is heated in an atmosphere of pure and dry hydrogen, the variation in the electrical resistance is regular, and the curve shows no angular points, but if the alloy is heated in moist hydrogen, it undergoes a very remarkable change. The colour becomes steel-grey or yellowish-grey, the tenacity increases from 65 kilos. to 80 kilos. (A. Le Chatelier), the elongation falls from 65 per cent. to practically *nil*, and the limit of elasticity becomes almost twice as great. The resistance becomes one-third less, and the curve shows a decided angular point at 550°, but above this temperature coincides with the normal nickel-iron curve. During cooling, there is a retardation of transformation from one modification to another similar to that produced by tempering, but this retardation may be avoided by very slow cooling. The alteration in the properties of the alloy is due to the oxidation of the silicon. C. H. B.

A Silver-Mercury Cell and its Relation to Temperature. By F. STREINTZ (*Ann. Phys. Chem.* [2], **38**, 514—534).—According to Helmholtz, the difference between the electrical and chemical energy of a cell is equivalent to the product of the absolute temperature with the change in potential difference with change of temperature, or, in other words, with the temperature coefficient of the cell. If the chemical is greater than the electrical energy, the temperature coefficient is negative, in the reverse case it is positive. Hence, from the nature of the temperature coefficient it may be at once seen whether the chemical energy is only partially converted into electrical energy, or if the electrical is in excess of the chemical energy (compare Jahn, Abstr., 1886, 840).

The author formerly observed that the cell Ag | Ag_2SO_4 | Hg_2SO_4 | Hg has an E.M.F. of zero at the ordinary temperature. This he now finds is due to the fact that a change in the temperature coefficient here takes place from positive to negative, this change taking place at a certain temperature, T_0, at which the potential difference $p_0 = 0$. Hence, if the cell be plunged into ice-cold water, the silver forms the positive pole, whereas in hot water the positive pole is formed by the mercury.

The author employs this cell in testing the above theory of Helmholtz, and finds a perfect agreement between the theoretical deductions and the results of his own experiments. H. C.

Batteries with Fused Electrolytes, and the Thermoelectric Forces at the Surface of Contact of a Metal and a Fused Salt. By L. POINCARÉ (*Compt. rend.*, **110**, 339—342).—The thermoelectric forces at the surface of contact of a metal with a fused salt are of the same order and sign as those observed by Bouty with saturated solutions. Employing the method of compensation, with the same metal and salt in two tubes at different temperatures, the thermoelectric force is practically independent of the absolute temperature, and proportional to the difference of temperature. With silver in silver nitrate, the hot metal is negative outside the cell; with zinc in zinc chloride,the warm metal is positive outside. If one of the salts solidifies, no change in the thermoelectric force is observed, and if the temperature is raised so high that the metal fuses, no electric change is observed at the moment of fusion. With a battery consisting of zinc in zinc chloride and tin in stannous chloride, the observed difference of potential is almost identical with that calculated from thermochemical data, and between 250° and 350° the E.M.F. of the battery is almost completely independent of the temperature, hence it may be concluded that, in accordance with Lippmann's theorem, the specific heat of the system is not altered by the passage of the electricity. In a similar battery in which one of the electrolytes remains solid whilst the other is fused, the E.M.F. varies notably with the temperature, a result also in agreement with Lippmann's theorem, the specific heat of the element varying with the changes of state which the current produces in the system.

Helmholtz's theory and its consequences hold good in case of batteries in which the electrolytes are made conducting, not by solution, but by igneous fusion. C. H. B.

Polarisation of Platinum Electrodes in Dilute Sulphuric Acid. By F. RICHARZ (*Ann. Phys. Chem.* [2], **39**, 67—88).—The polarisation of platinum electrodes in dilute sulphuric acid amounts to 2·5 dan. when the current-density is small, but with great current-density, values rising to 4·3 dan. have been found (Fromme, Abstr., 1888, 390). Such high results were doubted by the author, who subjected the methods by which they were obtained to a critical examination. He found that one or other of the assumptions on which Ohm's method is based (namely, that both the resistance of the electrolytic cell and the polarisation remain constant, although the

intensity of the current varies) must be incorrect. The same criticism applies to Buff's method, which assumes that the change of resistance in the cell with varying intensity is negligible with respect to the total resistance. On the assumption that the polarisation remains constant at 2·5 dan., the resistance for a current of 0·01 amp. is some eight times as large as the resistance for an intensity of 0·75 amp. This diminution of the resistance with increase of current may be partially accounted for by the heating of the electrolyte round the small electrode (a thin platinum wire) owing to the great current density. The heating may proceed so far as to surround a part of the electrode with a sheath of steam. Another cause of the change of resistance is the increasing difficulty of formation of gas bubbles on the electrode when the current is weak. Finally, there is the diminution of "transfer" resistance as the current increases (compare Sankey, this vol., p. 317). J. W.

Surface-tension of Polarised Mercury in Different Electrolytes. By F. Paschen (*Ann. Phys. Chem.* [2], **39**, 43—66).—Lippmann's capillary electrometer, whilst yielding excellent results for electromotive forces of less than 0·9 volt, is found by the author to be untrustworthy for values above this limit, on account of the polarisation caused by the liberation of hydrogen at the meniscus. In its stead he employs an open U-tube, one limb of which is about 24 mm. in diameter, the other about 3 mm. and shorter The tube should be so far filled with mercury that the meniscus nearly reaches the top of the narrow limb. The whole is immersed upright in a beaker containing dilute sulphuric acid and a layer of mercury, so that the meniscus in the shorter limb alone is below the surface of the liquid. Connection is made with the meniscus through the wide limb. This instrument, although not so delicate as Lippmann's, can be used for large electromotive forces. By its means the author investigated the change of surface-tension of mercury occasioned by polarisation in solutions of sulphuric acid, hydrochloric acid, sodium hydroxide, and various salts. He finds that all changes of surface-tension take place between the limits of +0·1 and −2 dan., and gives curves which show that up to the maximum it is the anion that exerts the decisive influence, whilst beyond the maximum it is the cathion. The position of the two characteristic points of the curves, the maximum and the point where electrolysis becomes evident, would appear to depend greatly on the concentration. The polarisation in Lippmann's electrometer, as well as in the instrument above described, seems to be entirely at the meniscus, and not at the large (anodic) mercury surface. When the polarisation attains a constant value, the surface-tension also becomes constant.

Temperature influences the results slightly, but not to such an extent as to interfere with the accurate working of the instruments under ordinary laboratory conditions. J. W.

Electrolysis of Fused Aluminium Oxide and Fluoride. By A. Minet (*Compt. rend.*, **110**, 342—343).—Electrolysis of aluminium oxide and fluoride by igneous fusion yields a quantity of metal

dependent on the time and the quantity of electricity acting. The yield varied in the experiments quoted from 50 to 70 per cent. of the theoretical quantity, and in one instance, with iron electrodes, was as high as 82 per cent. C. H. B.

Formation of Salts in Alcoholic Solution. By C. M. VAN DEVENTER and L. T. REICHER (*Zeit. physikal. Chem.*, 5, 177—180).—Since, according to the dissociation theory, the heat of neutralisation of an acid by a base in aqueous solution is not due to the combination of the negative and positive radicles, but is only that caused by the union of the hydrogen of the acid with the hydroxyl of the base, the authors propose to measure the heats of neutralisation of acids by bases in cases where dissociation cannot possibly take place. In this paper the results of the determination of the heat of neutralisation of acetic acid by potassium ethoxide in alcoholic solution are given, the number obtained being 7280 cals. The authors show that this number is in agreement with that which may be calculated from Berthelot's determination of the heat of neutralisation of acetic acid by potassium hydroxide in aqueous solution. H. C.

Thermochemical Properties of Silk. By L. VIGNON (*Compt. rend.*, **110**, 286—289).—Raw silk and silk freed from gum by treatment with soap were immersed in quantities of 9 to 12 grams in 500 c.c. of normal solutions of various compounds at 12°. The silk contained the average proportion of water, 10 per cent. The numbers represent the heat developed per 100 grams of silk:—

	H_2O.	KOH.	NaOH.	NH_3.	H_2SO_4.	HCl.	HNO_3.	KCl.
Raw....	0·10	1·35	1·55	0·65	0·95	0·95	0·90	0·20
Washed.	0·15	1·30	1·30	0·50	0·90	0·90	0·85	0·10

The heat developed is the sum of the chemical and physical changes which take place. The total heat developed by the raw silk in all the experiments is 13·15 Cals., and by the washed silk 11·95 Cals. It follows that the chemical energy of the silk-glue (grés) is greater than that of the fibroïn, the ratio being 1·451 : 1. More heat is developed by the action of acids and bases than by the action of neutral salts, and hence it would seem that silk-glue and fibroïn have decided basic and acidic functions. C. H. B.

Compounds which have a Tension of Dissociation equal to the Vapour-pressure of their Saturated Solution. By H. LESCŒUR (*Compt. rend.*, **110**, 275—276).—The behaviour of sodammonium and potassammonium as described by Joannis (this vol., pp. 209 and 560) is closely analogous to the behaviour of hydrated salts as observed by the author. All saline hydrates during a longer or shorter period of their definite existence afford examples of compounds the dissociation tension of which is equal to the vapour-pressure of their saturated solutions. The facts observed by Joannis are therefore not anomalous, and Roozeboom's hypothesis (this vol., p. 450) has no sufficient foundation. C. H. B.

Composition of the Vapour of Mixed Liquids. By A. WINKELMANN (*Ann. Phys. Chem.* [2], **39**, 1—5).—This research was undertaken to test the validity of the theoretical formulæ deduced by Planck (Abstr., 1888, 1146) to express the difference between the concentration of a solution of one liquid in another, and the concentration of the vapour given off by the solution. Concentration with respect to a certain substance is here taken to mean the ratio which the number of its molecules bears to the total number of molecules in the mixture, whether liquid or gaseous. The substances chosen by the author were water and propyl alcohol, and the method of experiment was either (1) to pass a slow current of dry air through the solution, kept at constant temperature, and collect the vapours in a vessel immersed in a mixture of solid carbonic anhydride and ether; or (2) to exhaust the flask containing the solution to such an extent that gentle ebullition took place, the vapours being condensed as before. Since the composition of the solution changes as the vaporisation proceeds, only relatively small quantities of the distillate could be collected, so that the composition of the latter had to be determined by a process of physical analysis, namely, by ascertaining the index of refraction. The results obtained with mixtures containing respectively 6·2 per cent. and 88·8 per cent. of propyl alcohol are considered by the author to be in satisfactory accordance with the formulæ, which, strictly speaking, hold good only for very dilute solutions. J. W.

Vapour-pressures of Solutions in Acetic Acid. By F. M. RAOULT and A. RECOURA (*Compt. rend.*, **110**, 402—405).—The vapour-tensions of acetic acid at various temperatures are as follows:—

t.	115°.	116°.	117°.	118°.	119°.	120°.
V. T.........	700·6	722·5	745·2	768·4	792·8	818·5

t.	121°.	122°.	123°.	124°.
V. T...............	844·2	871·0	898·2	925·6

The vapour-tensions of solutions of various substances in acetic acid were determined by the dynamical method, that is, by observing the boiling point under known pressures. This method can only be applied in somewhat concentrated solutions, but by means of other observations on solutions of various strengths, it is possible to calculate the reduction of vapour-tension in a very dilute solution (Abstr., 1888, 1145).

It has been shown that if f is the vapour-pressure of the solvent at a given temperature, f' its vapour-pressure at the same temperature when it holds a solid substance in solution, P the weight of the solid substance in 100 grams of the solvent, M the molecular weight of the solid, and M′ the molecular weight of the solvent, then, in very dilute solutions—

$$k = \frac{100(f - f')}{f\mathrm{P}}\frac{\mathrm{M}}{\mathrm{M}'},$$

k being a constant for each solvent. The value of k varies between 0·96 and 1·09, the mean being 1·05, and it is, therefore, practically

unity for every solvent. Taking $M' = 60$, or, in other words, assuming that the physical molecule of boiling liquid acetic acid is identical with the chemical molecule, the following values of k were obtained with various solids:—Nitronaphthalene 1·63, monobromcamphor 1·63, benzophenone 1·68, picric acid 1·60, salicylic acid 1·60, benzoic acid 1·59, diphenylamine acetate 1·57, potassium acetate 1·57, the mean being 1·61.

Acetic acid, therefore, presents an apparent anomaly. All analogy indicates, however, that at a given temperature the constitution of the physical molecule of a substance is the same in both the liquid state and the state of saturated vapour. If this be so, the molecular weight of boiling acetic acid will be 97, since the vapour-density of its saturated vapour at 118° is 3·35. If this value 97 is substituted for 60 in the calculation of the value of k, the mean result is practically 1·0, as in the case of all other solvents. The exception is, therefore, only apparent, and is correlated to the anomalous vapour-density of the acetic acid. C. H. B.

Influence of Capillarity and Diffusion on the Solvent Action of Liquids. By N. v. KLOBUKOFF (*Zeit. physikal. Chem.*, **5**, 181—190).—The author describes a number of experiments on the solvent action of liquids similar to those made by Spring (this vol., p. 328). He comes to conclusions with respect to the explanation of the phenomena observed which are in agreement with those of Bechhold (*loc. cit.*). H. C.

Nature of Osmotic Pressure. By J. H. VAN'T HOFF (*Zeit. physikal. Chem.*, **5**, 174—176).—A reply to the paper on the same subject by L. Meyer (this vol. p. 441). The author defends his view that the osmotic pressure is caused by the dissolved substance and not by the solvent, and supports it by the following argument. If we imagine nitrogen contained in a vessel of a material which it cannot permeate, but which is permeable by other gases, and this vessel be immersed in an atmosphere of hydrogen, the pressure of the hydrogen within and without the vessel will be the same, and any excess of pressure within the vessel will be due to the nitrogen which cannot permeate its walls. This will be true whatever the initial pressure and density of the hydrogen gas may be, and any change in this will in no way affect the excess of pressure within the vessel in magnitude, this latter being due solely to the nitrogen. Hence, if we imagine the pressure on the hydrogen increased until the gas is liquefied, the excess of pressure within the vessel will still remain the same, and will be that due to the nitrogen. But in this last case we must regard the hydrogen as the solvent and the nitrogen as the disolved substance, and the excess of pressure, which is what the author has called the osmotic pressure, is evidently due solely to the nitrogen, that is, to the dissolved substance. H. C.

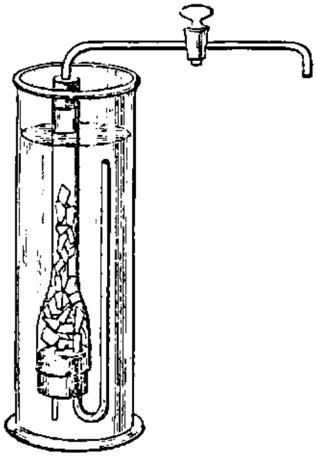
Stereochemical and Mechanical Views with reference to Single and Multiple Union of Atoms, and the Changes of One into the Other. By A. NAUMANN (*Ber.*, **23**, 477—484).—The carbon-

atom is regarded as occupying the centre of a regular tetrahedron, its attractions being exercised in the directions of the four solid angles. The line joining the centres of two such carbon-atoms with one another is assumed in each case to represent in magnitude and direction the resultant of the attractions by which the two atoms are held together. If in the case of a single bond the length of this line be taken as unity, then it follows geometrically that for a double bond the length will be 0·5774, and for a treble bond 0·3333; that is, the magnitude of the attraction in the first case being unity, in the second it will be $2 \times 0·5774$, and in the third $3 \times 0·3333$. Similar reasoning to the above may be employed in ascertaining the attractions of atoms other than carbon for one another. H. C.

Molecular Theory of a Substance formed from two different Components. By J. D. VAN DER WAALS (*Zeit. physikal. Chem.*, **5**, 133—173).—A mathematical paper not suitable for abstraction. H. C.

Apparatus for Fractional Distillation under Reduced Pressure. By E. VALENTA (*Zeit. anal. Chem.*, **28**, 673—676).—This apparatus was designed for the fractional distillation of substances which solidify at ordinary temperatures. The only novel portion is the receiver. This is a cylindrical vessel having at the top a tubulure to receive the end of the condenser tube, and a stopcock for connection with the pump. At the lower end the cylinder is narrowed to a tube which can be fitted into the necks of the flasks which are to receive the various fractions. This tube has a three-way tap, by which either the cylinder or the flask, or both, can be put in communication with the external air, so that the vacuum in the cylinder can be maintained while the flask is being changed. The cylinder is surrounded by a water-jacket, by which it can be kept at any convenient temperature. M. J. S.

Apparatus for Preparing Gases. By A. BURGEMEISTER (*Zeit. anal. Chem.*, **28**, 676).—A lamp-chimney is fitted with tubes as shown in the figure. The short straight one ending inside level with the lower cork is about 10 mm. in diameter, and projects 10—20 mm.



The bent tube is narrower, and projects inside 20—30 mm. above the cork. When the stopcock is opened, the acid enters by the narrow tube, and the heavier liquid produced by the reaction flows away by the short tube, and remains at the bottom of the outer vessel.

M. J. S.

Removal of Exhausted Solutions from Gas Apparatus. By A. C. Hertzog (*Zeit. anal. Chem.*, **28**, 678).—Instead of a separate syphon tube, the author uses a thistle-headed funnel which has a side tube branched in at a spot where the funnel tube is expanded into a bulb. The funnel can be shut off by a stopcock, and the gas pressure in the flask (when the gas outlet is closed) drives up the nearly exhausted liquid to the side tube, where it flows away.

M. J. S.

Inorganic Chemistry.

Action of Fluorine on Different Forms of Carbon. By H. Moissan (*Compt. rend.*, **110**, 276—279).—Chlorine does not combine directly with carbon even at very high temperatures, but fluorine and carbon combine with great energy even at the ordinary temperature. Lamp-black, purified and dried, immediately becomes incandescent; wood charcoal takes fire spontaneously, with projection of brilliant sparks. Denser forms of carbon must be heated to 50° or 100° before they will become incandescent. Ferruginous graphite from cast iron unites with fluorine below a dull red heat; Ceylon graphite, purified by fusion with potash, requires to be heated to a somewhat higher temperature; gas carbon burns in fluorine only at a red heat; the diamond is not affected when heated to redness in a current of fluorine. The products are gaseous, and are usually mixtures of different carbon fluorides.

The action of fluorine on an excess of one of the lighter forms of carbon, care being taken that the temperature does not rise very high, yields carbon tetrafluoride, CF_4, a colourless gas which liquefies under a pressure of 5 atmos. at 10°. Its sp. gr. agrees closely with the calculated number. Carbon tetrafluoride in contact with alcoholic potash yields potassium fluoride and carbonate. It is not decomposed by an electric spark, and is soluble in carbon tetrachloride, alcohol, benzene, and to a slight extent in carbon bisulphide. The gas can also be obtained by passing carbon tetrachloride vapour over silver fluoride heated at 300° in a glass or metal tube (compare Abstr., 1888, 1262).

The action of fluorine on carbon at a red heat yields a gaseous carbon fluoride which is not decomposed by electric sparks, is not absorbed by aqueous or alcoholic potash, is almost insoluble in water, but dissolves in alcohol. A small quantity of a solid product is obtained at the same time.

Both gaseous carbon fluorides yield a complex spectrum of lines and bands, amongst which the lines of fluorine are very distinct.

Guntz commenced the investigation of carbon fluorides, which he obtained by the action of carbon tetrachloride on metallic fluorides, but, at Berthelot's suggestion, relinquished the research in favour of Moissan. C. H. B.

General Method for the Preparation of Carbon Fluorides. By C. CHABRIÉ (*Compt. rend.*, **110**, 279—282; compare Moissan, preceding abstract).—Silver fluoride and carbon tetrachloride are heated together at 220° for two hours in sealed tubes of Bohemian glass. The glass is only slightly attacked. The product is carbon tetrafluoride, a gas which is only slightly soluble in water, but dissolves in benzene, and is absorbed by potassium hydroxide with formation of potassium carbonate and fluoride. Dicarbon tetrachloride yields dicarbon tetrafluoride, C_2F_4; sp. gr. = 3·43 (calc. = 3·46). C. H. B.

Vapour-densities of Selenium Chlorides. By C. CHABRIÉ (*Bull. Soc. Chim.* [3], **2**, 803).—When selenium tetrachloride is heated with chlorine in sealed tubes at 190—200° for 10—15 hours, it sublimes, and is deposited in well-defined crystals at the cooler end of the tube. The vapour-density, as determined by Meyer's method in an atmosphere of nitrogen at 360°, was found in two experiments to be 3·85 and 3·78 respectively, which corresponds with a dissociation occurring at that temperature, according to the equation—

$$2SeCl_4 = Se_2Cl_2 + 3Cl_2.$$

The vapour-density of selenium dichloride was found to be normal, the obtained values 7·69 and 8·123 agreeing closely with the calculated value 7·95. T. G. N.

Hydroxylamine Hydrochloride. By EICHKOFF (*J. Pharm.* [5], **21**, 245—246; from *Arch. Pharm.* [3], **27**, 713).—According to Raschig, the salt is obtained as follows:—A saturated solution of sodium nitrite (1 mol.) is added to a solution of hydrogen sodium sulphite (2 mols.) in a cooled vessel, and then a cold saturated solution of potassium chloride is added. In 24 hours hydroxylamine potassium disulphonate separates. This salt is boiled in water during several hours, and, on cooling, potassium sulphate is first deposited, and subsequently hydroxylamine sulphate. A solution of this salt, treated with the necessary amount of barium chloride, yields the hydrochloride, which can be obtained in colourless crystals, very hygroscopic, easily soluble in water and in alcohol. It melts at 151°, and decomposes at a higher temperature, yielding nitrogen, hydrogen chloride, ammonium chloride, and water. J. T.

Compounds of Hydroxylamine with Metallic Chlorides. By L. CRISMER (*Bull. Soc. Chim.* [3], **3**, 114—121).—Dihydroxylamine zinc chloride, $ZnCl_2,2NH_2\cdot OH$, is formed when zinc reacts with

hydroxylamine hydrochloride at 100°, or when an aqueous solution of the latter is treated with zinc sulphate and barium carbonate, or with zinc oxide or carbonate, as also when zinc chloride is added to an alcoholic solution of hydroxylamine hydrochloride. It is best prepared by dissolving hydroxylamine hydrochloride (10 parts) in strong alcohol (300 c.c.) contained in a reflux apparatus, and adding zinc oxide (5 parts) to the boiling solution; after a few minutes' ebullition, the clear liquor is decanted, and deposits, on cooling, dihydroxylamine zinc chloride as a white, crystalline powder. This substance is soluble in solutions of hydroxylamine hydrochloride, and is but slightly soluble in water and alcohol; it is alkaline to litmus, and its solutions decompose on evaporation, hydroxylamine being liberated. At 120°, it decomposes into zinc chloride, nitrous acid, ammonia, and hydroxylamine.

Dihydroxylamine cadmium chloride, $CdCl_2,2NH_2 \cdot OH$, may be prepared by any of the above methods, and forms brilliant crystals which are much more stable than those of the zinc compound.

Dihydroxylyamine barium chloride, $BaCl_2,2NH_2 \cdot OH$, is formed when barium carbonate reacts with a concentrated aqueous solution of hydroxylamine hydrochloride. It separates from its aqueous solution in large, tabular crystals.

Regarding dihydroxylamine zinc chloride as a combination of a dehydrating agent with anhydrous hydroxylamine, the author suggests its use for the preparation of aldoximes and of hydroxamic acids, and has already prepared acetoxime, camphoroxime, and acetohydroxamic acid by a simple reaction of the substance with acetone, camphor, and acetic acid respectively. T. G. N.

Combination of Ammonia and Hydrogen Phosphide with Silicon Chloride and Silicon Bromide. By A. BESSON (*Compt. rend.*, **110**, 240—242).—Ammonia is rapidly absorbed by silicon chloride with formation of the compound $SiCl_4,6NH_3$ described by Persoz in 1830. Silicon bromide acts less energetically, and must be left in an atmosphere of ammonia for 48 hours. The product $SiBr_4,7NH_3$ is an amorphous, white solid, similar in appearance to the chlorine compound. It is decomposed by water with formation of an alkaline solution smelling strongly of ammonia.

Hydrogen phosphide is not absorbed by silicon chloride at the ordinary temperature, but at −23°, the chloride absorbs about 20 vols. of the gas, which are given off unchanged if the temperature is raised to 20°. At −50°, 40 vols. of hydrogen phosphide are absorbed, with formation of a compound $SiCl_4,2PH_3$, which remains liquid even at −60°. Under a pressure of 20 atmos. at 16°, hydrogen phosphide and silicon chloride yield small, highly refractive crystals, which disappear when the pressure falls to 15 atmos. At 0°, the crystals appear under 15 atmos., and disappear when the pressure falls to 10 atmos.; at −23°, they appear under 5 atmos., and remain after the pressure is removed; at −35°, the crystals form under the ordinary pressure. The composition of this compound could not be determined; it is formed from the vapour of the chloride, and is never formed in the liquid.

Silicon bromide is without action on hydrogen phosphide under the ordinary pressure, even at a temperature at which it solidifies. After repeated compression and maintenance of the pressure for several hours, a colourless liquid forms, which becomes white and opaque and changes into an amorphous, white solid. C. H. B.

Compounds of the Alkali Metals and Ammonia. By JOANNIS (*Compt. rend.*, **110**, 238—240).—The author has previously found (this vol., p. 209) that the vapour-pressure of a solution of sodium in liquid ammonia varies until the composition $Na + 5{\cdot}3NH_3$ is reached, then remains constant until solid sodammonium separates, the complete removal of ammonia being followed by the dissociation of the sodammonium.

The method adopted enabled a difference of pressure of 0·2 mm. to be recognised. At 0° the tension remained constant; at —10° it remained constant, whilst the composition varied from $NaNH_3 + 0{\cdot}46NH_3$ to $0{\cdot}19NaNH_3 + 0{\cdot}81Na$; at 22·4° the tension was constant, although the composition varied from $NaNH_3 + 2{\cdot}42NH_3$ to $0{\cdot}67NaNH_3 + 0{\cdot}33NH_3$. At the different temperatures the volatilisation of the ammonia left a crystalline residue of sodammonium, and not of sodium alone. Similar results were obtained with potassammonium between 0° and +8·44°.

Roozeboom's hypothesis (this vol., p. 450) requires unequal pressure below 0°, and the decomposition of the saturated solution into sodium and ammonia above 0°, without the appearance of any solid sodammonium. C. H. B.

Blue Flame produced by Common Salt in a Coal Fire. By G. SALET (*Compt. rend.*, **110**, 282—283).—The well-known blue flame which is produced when common salt is thrown into a coal or coke fire, and which A. P. Smith attributed to hydrogen chloride (Abstr., 1879, 497) is due to cupric chloride, and its spectrum (*loc. cit.*) corresponds with the second spectrum of the chloride as described by de Boisbaudran. Copper was readily detected in the ash of the coke used by a delicate method which is generally applicable. The copper in the solution is deposited on the point of a needle, and if the latter is held in a bunsen flame, no coloration is produced, but when hydrochloric acid is volatilised in the flame, the green colour of the copper chloride becomes visible. The reaction is very delicate. The volatilisation of hydrochloric acid in a flame for this and similar purposes is readily effected by introducing into the flame a bundle of very fine platinum wire which has been dipped in the acid. It is easy to arrange this bundle so that the acid is supplied to the flame continuously. C. H. B.

Ammonium Borofluoride. By F. STOLBA (*Chem. Centr.*, 1890, i, 211—212, from *Chem. tech. Centralanzeig.*, **7**, 459—460).—Ammonium borofluoride is prepared by saturating commercial hydrogen fluoride with boric acid, and then adding ammonia to alkaline reaction. The silicic acid contained in the commercial hydrofluoric acid is precipitated and is filtered off, and the filtrate allowed to cool, when ammonium

borofluoride crystallises out. It may be purified by recrystallisation from water. When heated in a platinum dish, it completely volatilises; the freshly prepared solution has a slightly acid reaction to litmus. The aqueous-alcoholic solution burns without any green flame. It has only slightly antiseptic properties, and is not nearly so poisonous as the silicofluoride. Its density = 1·851 at 17·5°. It is soluble in 4 parts of water at 16°, and in 1·02—1·05 parts of boiling water. J. W. L.

Silver. By J. S. STAS (*Chem. Centr.*, 1890, i, 87; from *Bull. Acad. roy. Belg.* [3], **18**, 23).—At the request of Dumas, the author has repeated all his experiments on silver. He finds that the metal is slightly volatile at a low red heat in a vacuum, but not at this temperature under the ordinary atmospheric pressure, nor in a vacuum at 440—450°. Finally, he finds that the silver which he used in his atomic weight determinations contained gases, but that their quantity was altogether insignificant ($\frac{1}{35800}$ by weight), and the error caused thereby could not affect the results to any greater extent than those errors which are unavoidable in such experiments. J. W. L.

Barium, Strontium, and Calcium Plumbates. By G. KASSNER (*Arch. Pharm.* [3], **28**, 109—115).—Equal weights of barium hydroxide and lead oxide, when heated together while exposed to air, give a new black compound, barium plumbate, Ba_2PbO_4; a mixture of lead oxide (1 mol.) and barium carbonate (2 mols.), heated to bright redness, gives the same compound, but the temperature required is much higher than with the hydroxide, where it can be produced in the bunsen flame. Similarly, strontium carbonate gives a salt of a chocolate-brown colour, whilst calcium plumbate is formed from the carbonate at a comparatively low temperature, that of a bunsen flame sufficing. The calcium mixture remains pulverulent to the end, and the plumbate forms a heavy, yellowish-red powder, scarcely distinguishable in appearance from powdered lead oxide. The three new compounds are entirely insoluble in water; but on long standing the water becomes alkaline, and a skin of alkaline carbonate forms on the surface. They are all decomposed by acids: in the case of hydrochloric acid, with evolution of chlorine; other acids cause the precipitation of lead peroxide, which may be looked on as the anhydride of orthoplumbic acid, H_4PbO_4. To obtain a clear solution of the three compounds in acid, a reducing agent is necessary, such as oxalic acid, sugar, &c. Nitric acid and hot acetic acid are most suitable for this purpose. Carbonic anhydride in the presence of moisture decomposes the plumbates. The alkaline hydrogen carbonates decompose them with considerable increase of temperature and formation of alkaline hydroxide, which is free from lead when excess of lead oxide has been avoided in preparing the plumbate. Finally, water alone under high pressure and increased temperature produces considerable decomposition. If ammonium salts are added to the water, ammonia is set free, a salt of the earth is produced and lead peroxide; if the salt be soluble, lead peroxide can thus be obtained in a pure form. J. T.

Sodium Beryllium Silicates. By P. HAUTEFEUILLE and A. PERREY (*Compt. rend.*, **110**, 344—346; compare Abstr., 1889, 104).—A mixture of beryllia, silica, and sodium oxide, in the same proportions as in beryllium nepheline, when heated with excess of normal sodium vanadate at about 800°, yields crystals which, when purified by treatment with hot water and levigation, have the composition

$$3SiO_2,Be_2O_3,Na_2O.$$

The crystals are hexagonal prisms terminated by well-developed hexagonal prisms, are birefractive, uniaxial, and negative, and have a conchoidal fracture. They have a blue or green coloration, due to minute quantities of vanadium, melt easily before the blowpipe, and are slowly attacked by concentrated acid in the cold.

If the three oxides are mixed in proportions corresponding with the preceding product and treated in the same way, they yield a new compound which has the composition of an albite, $6SiO_2,Be_2O_3,Na_2O$, crystallises in monoclinic prisms with modified angles, and is not attacked by acids.

Silica in the proportion of $4·5SiO_2$ to Be_2O_3, yields rhombic prisms of the composition 20·67 to $22·41SiO_2,3Be_2O_3,2Na_2O$.

A mixture in the proportion $2SiO_2 + Be_2O_3 + 1·5Na_2O$ yields a mixture of the two compounds $3SiO_2,Be_2O_3,Na_2O$ and

$$15SiO_2,2Be_2O_3,3Na_2O.$$

They crystallise together, and can be separated by treating the crystals with hydrochloric acid and then levigating with a solution of cadmium tungstoborate.

A mixture of $7SiO_2$, Be_2O_3, $1·5Na_2O$ yields rhombic prisms of the compound $18SiO_2,2Be_2O_3,3Na_2O$, which has the same form as the compound containing $15SiO_2$.

With sodium tungstate instead of vanadate, the compounds $14SiO_2,2Be_2O_3,3Na_2O$ and $18SiO_2,2Be_2O_3,3Na_2O$ are obtained.

C. H. B.

Action of Potassium and Sodium Arsenates on Oxides of the Magnesium Series at High Temperatures. By C. LEFÈVRE (*Compt. rend.*, **110**, 405—408).—Magnesium carbonate or oxide dissolved at a low temperature in excess of fused potassium metarsenate yields a pyroarsenate, $4MgO,2K_2O,3As_2O_5$, crystallising in transparent prisms with angles of extinction at 45° from the axis. If the metarsenate is saturated with the oxide at a higher temperature, the orthoarsenate, $2MgO,K_2O,As_2O_5$, is obtained; it is analogous to the phosphate formed under similar conditions. In presence of potassium chloride, the same product is obtained if the proportion of chloride does not exceed 85 per cent., but with a higher proportion, chlorine compounds are formed. Potassium pyroarsenate and orthoarsenate in presence of potassium chloride yield the same compound; it crystallises in foliated lamellæ with longitudinal extinction.

At low temperatures, without excess of oxide, sodium metarsenate yields the pyroarsenate, $4MgO,2Na_2O,3As_2O_5$, in the form of large, transparent lamellæ, which act only slightly on polarised light. At higher temperatures, and with a greater proportion of oxide, the

product is the orthoarsenate, $2MgO,Na_2O,As_2O_5$. Sodium pyroarsenate and orthoarsenate yield the same product, and it is also formed in presence of sodium chloride; it crystallises in large, transparent prisms which show longitudinal extinction and dissolve slowly in dilute acids.

Zinc oxide in excess of potassium metarsenate yields the compound $2ZnO,As_2O_5$ in small lamellæ which act on polarised light and are slowly altered by water. With excess of zinc oxide, the product is $2ZnO,K_2O,As_2O_5$, which is also formed in presence of potassium chloride in any proportion. Potassium orthoarsenate and pyroarsenate yield the same product; it crystallises in small, slightly opaque prisms, with longitudinal extinction. Sodium metarsenate at low temperatures yields the compound ZnO,Na_2O,As_2O_5, which acts energetically on polarised light. With excess of zinc oxide at a higher temperature, the product is $2ZnO,Na_2O,As_2O_5$, which is also formed in presence of sodium chloride; it crystallises in elongated, transparent prisms with longitudinal extinction.

Manganese carbonate, or one of the oxides, dissolved in excess of potassium metarsenate, yields the compound $2MnO.As_2O_5$, isomorphous with the corresponding product from zinc. With excess of manganese, the product is $2MnO,K_2O,As_2O_5$, which is also formed in presence of potassium chloride in proportion not exceeding 88 per cent. With a higher proportion of the chloride, chlorine compounds are obtained. Potassium pyro- and ortho-arsenate yield the same compound; it crystallises in rose-coloured prisms, and is isomorphous with the corresponding magnesium compound. Sodium metarsenate yields the compound $2MnO,4Na_2O,3As_2O_5$ in small, colourless crystals with oblique extinction. In presence of sodium chloride, the same product is obtained, together with the compound $MnO,2Na_2O,As_2O_5$, which is the sole product when the orthoarsenate or pyroarsenate is employed, and crystallises in small, transparent, rose-coloured crystals without action on polarised light.

Cadmium oxide, or carbonate, and potassium metarsenate yield the product $2CdO,As_2O_5$, or if the oxide is in excess, $2CdO,K_2O,As_2O_5$, isomorphous with the corresponding zinc compound. No chlorine-products are formed even in presence of large quantities of potassium chloride. Sodium arsenates yield the products $2CdO,4Na_2O,As_2O_5$ and $CdO,2Na_2O,As_2O_5$, isomorphous with the corresponding manganese compounds.

Nickel oxide dissolved in potassium metarsenate to the extent of 8 per cent. yields the compound $12NiO,3K_2O,5As_2O_5$ in prisms, which are probably rhombic. With a higher proportion of nickel, the product $2NiO,K_2O,As_2O_5$ is obtained at the same time, and in presence of potassium chloride it is the only product; it crystallises in large, pale-yellow, micaceous lamellæ which depolarise light feebly. Sodium metarsenate yields green, transparent, monoclinic prisms of the pyroarsenate, $4NiO,2Na_2O,3As_2O_5$. In presence of sodium chloride, the compound $2NiO,Na_2O,As_2O_5$ is also obtained; the latter is the sole product when sodium pyroarsenate or orthoarsenate is used; it crystallises in green lamellæ derived from a hexagonal prism.

Cobalt oxide in small quantity in potassium metarsenate is con-

verted into violet mamillary crystals of the compound $2CoO,As_2O_5$, which act on polarised light. With more cobalt oxide, the product $2CoO,K_2O,As_2O_5$ is obtained in slightly opaque, blue prisms with longitudinal extinction. This compound is the sole product in presence of potassium chloride. Sodium metarsenate yields the compound $4CoO,2Na_2O,3As_2O_5$ in violet, strongly macled lamellæ, isomorphous with the corresponding compound of nickel. In presence of sodium chloride, the compound $CoO,2Na_2O,As_2O_5$ is also formed, and it is the only product when sodium orthoarsenate or pyroarseuate is used; it forms blue, transparent crystals, isomorphous with those of the corresponding manganese and cadmium compounds.

With the potassium arsenates, all the oxides yield as the ultimate product a compound with the formula $2MO,K_2O,As_2O_5$. With the sodium arsenates, magnesium, zinc, and nickel yield a similar product, but cobalt, cadmium, and manganese yield a compound $MO,2Na_2O,As_2O_5$. C. H. B.

Thiosulphates. By A. Fock and K. Klüss (*Ber.*, **23**, 534—541; compare this vol., p. 330).—The solid manganese thiosulphate described by Vortmann and Padberg (this vol., p. 12) could not be obtained by the authors; the reddish oil which is precipitated on adding alcoholic ether to its solutions decomposes into sulphur and manganese sulphite.

Cadmium thiosulphate, $CdS_2O_3 + 2H_2O$, is obtained in crystals when a solution of strontium thiosulphate is treated with cadmium sulphate, the filtrate mixed with alcoholic ether and kept for some time. It does not lose its water over sulphuric acid, but it gradually decomposes into cadmium sulphide and sulphate on keeping, with liberation of sulphurous anhydride.

The salt $NH_4S{\cdot}SO_2{\cdot}OK$ crystallises in small, colourless, monosymmetric plates, $a : b : c = 1{\cdot}3547 : 1 : 0{\cdot}8521$; when boiled with water and ethyl bromide, it yields potassium ethyl thiosulphate, $SEt{\cdot}SO_2{\cdot}OK$. The salt $SK{\cdot}SO_2{\cdot}ONH_4$ could not be obtained.

Potassium magnesium thiosulphate, $K_2S_2O_3,MgS_2O_3 + 6H_2O$, forms large, transparent, monosymmetric crystals, $a:b:c = 2{\cdot}0001 : 1 : 0{\cdot}4744$; it is not deliquescent, and does not lose weight when kept over sulphuric acid.

The ammonium magnesium salt, $(NH_4)_2S_2O_3,Mg_2S_2O_3 + 6H_2O$, crystallises in monosymmetric prisms, $a : b : c = 0{\cdot}6422 : 1 : 0{\cdot}9238$, is stable in the air and does not lose water over sulphuric acid.

F. S. K.

Saturated Solutions of Compounds of Cupric and Potassium Chlorides. By W. Meyerhoffer (*Zeit. physikal. Chem.*, **5**, 97—132).—In a former paper (Abstr., 1889, 819), the author has shown that two compounds of cupric and potassium chlorides, $CuCl_2,2KCl + 2H_2O$ and $CuCl_2,KCl$, are capable of existing in the solid form. A determination of the solubility of the compounds of cupric and potassium chlorides at temperatures from 0° to 100°, and an examination of the curves obtained, show that between the three substances $CuCl_2$, KCl, and H_2O the following conditions of equilibrium may exist.

First Group: Two substances and three phases—

1.	KCl	+	solution	+	vapour.
2.	$CuCl_2,2H_2O$	+	,,	+	,,
3.	$CuCl_2,KCl$	+	,,	+	,,
4.	$CuCl_2.2KCl,2H_2O$	+	,,	+	,,

Second Group: Three substances and four phases—

5.	$CuCl_2,2KCl,2H_2O$	+	KCl	+	solution	+	vapour.
6.	$CuCl_2,KCl$	+	KCl	+	,,	+	,,
7.	$CuCl_2.2KCl,2H_2O$	+	$CuCl_2,2H_2O$	+	,,	+	,,
8.	$CuCl_2,KCl$	+	$CuCl_2,2H_2O$	+	,,	+	,,
9.	$CuCl_2,KCl$	+	$CuCl_2,2KCl,2H_2O$	+	solution	+	vapour.

H. C.

Crystalline Mercury Oxychloride and Estimation of Mercury. By J. VOLHARD (*Annalen*, **255**, 252—256).—Mercury oxychloride, $Hg_3O_2Cl_2$, can be easily prepared by treating a cold saturated solution of mercuric chloride with sodium acetate. After keeping for some days, crystals are deposited together with a colourless, flocculent compound which can be easily separated; when no further separation of the oxychloride occurs, a solution of potassium hydrogen carbonate is added, in small quantities at a time, whereon a further crop of crystals is obtained. The crystals are monoclinic, $a : b : c = 0·9178 : 1 : 0·9978$, $\beta = 65° 30'$; they are anhydrous, and when crushed form a reddish-brown powder. Mercury oxychloride is insoluble in water, but readily soluble in acids; it is converted into the red oxide when treated with alkalis. When heated carefully, mercury chloride sublimes, leaving almost pure oxide.

Mercury sulphide is completely precipitated from its solution in alkalis on the addition of ammonium salts; this reaction can be employed for the estimation of mercury as follows:—The solution of mercury, which must be in the mercuric condition, is partially neutralised with sodium carbonate, treated with a slight excess of a concentrated, freshly prepared solution of ammonium sulphide, and pure sodium hydrate added, with constant shaking, until the solution commences to become transparent. The whole is then boiled, the addition of soda continued until the sulphide has completely dissolved, and then a solution of ammonium nitrate added to the boiling solution until the sulphide is completely reprecipitated. After boiling until the ammonia is almost completely expelled, the precipitate is allowed to settle, washed by decantation with boiling water until the washings give no reaction with silver solution, then transferred to a weighed filter, dried, and weighed. If the boiling has been continued so long that the precipitate may be contaminated with sulphur, a little sodium sulphite is added, and the solution boiled again.

By this method mercury can be estimated as sulphide much more conveniently, accurately, and quickly than by precipitation with hydrogen sulphide. F. S. K.

History of the Rare Earths. By L. DE BOISBAUDRAN (*Bull. Soc. Chim.* [3], **3**, 53—67).—A lengthy controversial paper, in which the

author criticises some of the statements made by Mr. Crookes in his presidential address (Trans., 1889, 269). The author considers the substances denoted as Z_α and Z_β to be quite distinct from "yttria," both as regards their atomic weights and their chemical properties, and that they are actively fluorescent, and do not give the yttria spark spectrum. Further, he replies to Crookes in reference to reversion spectra, the gadolinium question, and the fluorescence of alumina.

T. G. N.

Constitution of Manganese Peroxide. By W. SPRING and M. LUCION (*Bull. Soc. Chim.* [3], 3, 4—8).—From the fact that when barium peroxide is triturated with a slight excess of crystalline manganous chloride, oxygen is evolved and manganic sesquioxide is formed, it would seem that the molecular structure of manganese peroxide differs from that of barium peroxide.

When barium manganate is heated with a solution of manganous sulphate at 100° for a week, manganese peroxide is obtained, and from this method of formation it may be regarded as a manganous manganate, $MnMnO_4$.

At a high temperature, sodium manganate and manganous carbonate react without evolution of oxygen to form manganese sesquioxide. Manganese peroxide, when heated with sodium hydroxide in an atmosphere of nitrogen, leaves a residue of manganese sesquioxide, and not of manganese peroxide, and from this fact the authors conclude that manganous oxide is formed in the reaction and unites with manganese peroxide, thus—$MnO + MnO_2 = Mn_2O_3$, and they consider this relationship is substantiated, since manganese sesquioxide reacts with dilute nitric acid to produce manganous nitrate and manganese peroxide—$Mn_2O_3 + 2HNO_3 = Mn(NO_3)_2 + MnO_2 + H_2O$.

The authors conclude that the formula for manganese peroxide should be doubled, and Mn_2O_4 would then represent a manganous manganate, $MnMnO_4$.

T. G. N.

Influence of certain Foreign Metals on the Properties of Steel. By F. OSMOND (*Compt. rend.*, 110, 242—245).—It is known that while iron cools from a high temperature, two distinct developments of heat take place, one, a_3, which causes the temperature to remain at 855° for a long time, and is due to the conversion of the allotropic modification Feβ into the modification Feα; the other, a_2, at about 730°, much less strongly marked and possibly due to another allotropic change, possibly merely the final stage of a_3 which has been retarded by the presence of carbon. In addition to these, there is the change a_1, or recalescence, due to the conversion of tempered carbon into annealed carbon.

Boron.—Iron containing boron was prepared by Roberts-Austen by fusing the metal with crystallised boron in a vacuum. The boron behaves in the same manner as carbon; a_3 is lowered and takes place at 815—805°, and partly at 735—725°, or becomes partially coincident with a_2.

Nickel, in quantity varying from traces to 5·97 per cent., the proportion of carbon being 0·34 per cent. In similar steel free from nickel a_3

and a_2 are coincident, but remain quite distinct from a_1. When the steel contains nickel, a_3, a_2, and a_1 coincide at 660—640°, a point distinctly below the normal temperature of recalescence. Hopkinson has observed that with a steel containing 25 per cent. of nickel, the critical point remained below 0° during the whole period of cooling. The effect of nickel is similar to that of manganese.

Copper.—Samples prepared by Ball and Wingham had the following composition—

	1.	2.	3.
Copper	0·847	4·10	4·44
Carbon	0·102	0·183	0·10

As the proportion of copper rises, a_3 and a_2 are lowered, and with the quantity present in samples 2 and 3, a_3 and a_2 coincide at 730—720°, whilst a_1 takes place at 625—600°. Copper has the same effect as carbon, but in a lower degree; its influence on recalescence is similar to that of manganese and nickel.

Silicon.—With specimens prepared by Hadfield, as the proportion of silicon increases the quantity of heat liberated during a_3 decreases, and with 2 per cent of silicon is practically *nil.* Moreover, the evolution of heat does not take place at a lower temperature as with carbon, manganese, nickel or copper, and it follows that silicon prevents the conversion of Feα into Feβ; the other elements enumerated tend to keep the iron in the form of Feβ during cooling. a_2 is as well marked as usual, but takes place at 730—720° or 710—700°. a_1 is also distinct, but takes place at a higher temperature, 660° to 650° or 710° to 700°.

Arsenic, varying in quantity from traces to 0·55 per cent. in specimens prepared by Harbord and Tucker, raises the temperature at which a_3 occurs, and makes the phenomenon less distinct. It has no effect on a_2 and a_1, and hence resembles silicon in its action.

Tungsten, in proportion varying from traces to 1·5 per cent., has no effect on a_3, but if the metal has been sufficiently strongly heated it lowers a_1 very considerably, recalescence taking place at 540—530° in the most marked instance. C. H. B.

Influence of Foreign Substances on Iron and Steel: Relation between their Atomic Volume and the Allotropic Modifications of Iron. By F. OSMOND (*Compt. rend.*, **110**, 346—348; compare preceding abstract).—The elements present in the irons and steels which the author has used in his researches on the allotropic modifications of iron may be classed in two groups, according to their atomic volumes.

Element.	Carbon.	Boron.	Nickel.	Manganese.	Copper.
At. vol. ..	3·6	4·1	6·7	6·9	7·1

Element.	Chromium.	Tungsten.	Silicon.	Arsenic.	Phosphorus.	Sulphur.
At. vol. ..	7·7	9·6	11·2	13·2	13·5	15·7

Other conditions being the same, the elements in the first group, which have an atomic volume less than that of iron, 7·2, retard the con-

version of Feβ into Feα, and that of "tempered carbon" into "annealed carbon," and hence, if the rate of cooling is equal, they increase the proportion of Feβ in the cooled metal and consequently its hardness. They are, therefore, equivalent in their effect to a higher or lower degree of tempering.

Metals with a higher atomic volume than iron, on the other hand, tend to raise, or to keep at its normal temperature, the conversion of Feβ into Feα, and hence they render the reverse change more or less incomplete during heating, and hasten, as a rule, the conversion of tempered carbon into annealed carbon. They therefore keep the iron in the α condition at high temperatures and also at low temperatures, and their presence in the iron would be one cause of softness and malleability, resembling in this respect the operation of annealing, if it were not that their own properties and those of their compounds produce strongly marked secondary effects.

The connection between the atomic volume of a metal and its effect on iron is similar to that found by Roberts-Austen to exist between the atomic volumes of elements and their effect on gold (*Phil. Trans.*, **179**, 339—349). C. H. B.

Action of Sodium Carbonate and Bromine on Solutions of Cobalt and Nickel Salts. By J. GIBSON (*Proc. Roy. Soc. Edin.*, **17**, 56—58).—When sodium carbonate is added in large excess to a solution of a cobaltous salt, and the mixture shaken with a sufficient quantity of bromine, the whole of the precipitated cobaltous carbonate dissolves to a dark-green solution, stable at ordinary temperatures, cobaltic oxide being precipitated on the addition of aqueous alkalis. If this green liquid is acidified with sulphurous anhydride, and the decolorised solution then rendered alkaline, a red-coloured solution is produced, which absorbs oxygen from the air, and again becomes green.

If excess of sodium carbonate is added to a solution of nickel, the resulting mixture behaves differently on addition of bromine, according to the quantity of bromine added. If a large excess of bromine is added, part of the nickel goes into solution, part remains undissolved as pale-green carbonate; if a smaller proportion of bromine is added, so as to have excess of sodium carbonate, the nickel is completely converted into peroxide.

The author hopes, by making use of these peculiarities, to devise a rapid and effectual method of separating the two metals.

E. W. P.

Chrome Iron. By S. MEUNIER (*Compt. rend.*, **110**, 424—426).—When a mixture of ferrous chloride and chromic chloride in suitable proportions is heated to redness in a porcelain tube in an atmosphere of hydrogen, a silvery-white, distinctly magnetic metal is obtained, which is not attacked by boiling concentrated nitric or hydrochloric acid, and only very slightly by aqua regia. It has the composition Fe 35·01, Cr 64·80 = 99·81. This alloy is found in the porcelain boat (used to contain the chlorides) in the form of irregular, highly crystalline tubercles, and the interior of the tube is coated with the alloy, which, when in very thin layers, takes dendritic forms.

If this alloy is heated to redness in a current of steam, it is completely oxidised and yields chromite of sp. gr. 4·48, identical in all its properties with the natural mineral.

The alloy can be obtained in concretions round particles of minerals contained in the porcelain tube, and these concretions can be converted into chromite by the action of steam. The author concludes that chromite and analogous minerals have been produced in a similar way from metallic alloys formed in the depths of the earth and brought up into the water-bearing layers of the earth's crust by mechanical forces. C. H. B.

Mineralogical Chemistry.

Native Gold in Calcite. By J. S. DILLER (*Amer. J. Sci.* [3], 39, 160).—At a mine on Digger Creek, Minersville, Trinity Co., California, excellent specimens have been obtained of gold associated with calcite. The calcite occurs in irregularly distributed, small, lenticular masses in a dark, carbonaceous shale. It is not always auriferous, but is occasionally very rich in gold. Quartz has also been found in the mine, but it is less abundant than the calcite, and is rarely auriferous. In the bed containing the calcite, as well as in the metamorphosed beds of the auriferous slate series below it, considerable quantities of iron pyrites occur. This may, perhaps, have been the source of the gold. B. H. B.

Lussatite, a new form of Silica. By E. MALLARD (*Compt. rend.*, 110, 245—247).—Transparent crystals of quartz associated with bitumen at Pont-du-Château are frequently covered with a translucent envelope, which does not hide the form of the crystals, but rounds off their edges and solid angles. It consists of very small nodules with a fibro-lamellar structure, the fibres being perpendicular to the face of the enclosed crystal. These fibres are less birefractive than quartz, extinguish almost exactly along their length, and the sign of their optical elongation is positive; their sp. gr. is 2·04. The optical elongation of chalcedony is always negative; it is more strongly birefractive, and its sp. gr. is 2·59. The sp. gr. of tridymite is 2·22, of opal 1·93 to 2·09. The refractive index of the new mineral for D is 1·446, being almost identical with that of opal and distinctly lower than that of tridymite. It is practically pure silica, but loses 8·1 per cent. of water above 600°. After ignition, its sp. gr. is reduced to 1·94, and the grains have become white and almost opaque, but the fibres retain their birefractive power and the sign of optical elongation remains positive.

This new form of silica, which the author proposes to call *lussatite*, from one of its localities, is never quite pure, but is usually intimately associated with opal, to the presence of which the loss on

ignition is probably due. It occurs in concretions consisting mainly of opal; in yellowish stalactitic chalcedony; with opal in the yellowish silica from the Faroe Islands; and probably in many other localities. C. H. B.

Minium from Leadville. By J. D. HAWKINS (*Amer. J. Sci.* [3], **39**, 42—43).—Minium from the Rock Mine, Leadville, gave on analysis—

Insol.	Pb_3O_4.	Fe_2O_3.	V_2O_3.	Total.
7·51	91·39	0·80	0·52	100·22

The portion insoluble in hydrochloric acid contained—

SiO_2.	Al_2O_3,Fe_2O_3.	CaO.	PbS.	Total.
2·00	0·41	0·28	5·08	7·77

The mineral has a sp. gr. of 4·55. Its hardness is 2·5, fusibility 1, lustre dull, colour bright-red, streak orange-red, and fracture cubical. The cubical fracture and the occurrence in the minium of galena suggest that the mineral is a pseudomorph after galena.

B. H. B.

Corundum in Patrick Co., Virginia. By F. A. GENTH (*Amer. J. Sci.* [3], **39**, 47—50).—On a hill near Stuart, Patrick Co., Virginia, corundum and associated minerals were found on the surface. The rocks of the district are mica schists, chloritic schists, and slates, intersected by several granite dykes. Neither serpentine nor olivine rock has been observed in connection with the corundum. This occurrence of corundum is thus entirely different from any previously described. Only a small quantity of the mineral has been found. Sometimes only microscopic grains of the corundum are left disseminated in the materials resulting from its alteration, namely, andalusite, cyanite, mica, and chloritoid. The alteration of corundum into andalusite has never been observed before. B. H. B.

Manganese Oxides: Psilomelanes and Wads. By A. GORGEU (*Compt. rend.*, **110**, 247—249).—Three samples of psilomelane, from Romanèche, Thuringia, and Lorca, in Spain, were examined with a view to determine their constitution. That from Romanèche was the richest in barium, but the composition of the different layers of the mineral differed considerably. In psilomelanes generally, the higher oxides of manganese are not present in the form of dioxide, but in the form of manganous manganites, such as $MnO,6MnO_2$ and $MnO,8MnO_2$. The basic oxides are variable; manganous and barium oxides in the mineral from Romanèche; manganous, barium, calcium, and potassium oxides in that from Thuringia; manganous, barium, and sodium oxides in that from Lorca. All the psilomelanes are hydrated, and the most basic have the composition $RO,3MnO_2$.

Wads from Romanèche, Giessen, and another locality were examined. Two of them were found to be crystalline, a fact which has not been observed before. The crystals were so small that their form could not be determined, but it was proved that they act distinctly on

polarised light. Like the psilomelanes, they are manganites with variable bases, their composition oscillating between $MnO,7MnO_2$ and $MnO,10MnO_2$. One of the crystalline specimens, from Romanèche, had almost exactly the composition $RO,3MnO_2 + H_2O$, and the other, locality unknown, the composition $RO,3MnO_2 + 3H_2O$, and they are therefore closely analogous to the more basic psilomelanes.

The energy of the acidic function of the manganic peroxide is shown by the fact that when finely-powdered psilomelanes or wads are boiled with nitric acid diluted with 4 vols. of water, only a very small proportion of the basic oxides is dissolved even in the case of the specimens richest in barium. C. H. B.

Composition of Saline Sublimates at Vesuvius. By G. FREDA (*Gazzetta*, **19**, 16—21).—The analyses here given confirm Scacchi's view that these sublimates often contain a larger percentage of potassium than of sodium chloride. The author ascribes the origin of the potassium chloride to the substitution underground of soda for potash in the molten silicates of potassium by the action of infiltrated sea-water and to the greater volatility of potassinm chloride. This substitution may also account for the variations in the composition of leucite from different lavas. S. B. A. A.

Lansfordite and Nesquehonite. By F. A. GENTH and S. L. PENFIELD (*Amer. J. Sci.* [3], **39**, 121—137).—Under the name of lansfordite, Genth (Abstr., 1888, 793) described a new mineral discovered in one of the anthracite miues near Lansford, Pennsylvania. Analysis gave results corresponding with the formula $3MgCO_3,Mg(OH)_2 + 21H_2O$. Where the crystals were attached to the carbonaceous shales, groups of transparent, white, radiating prismatic crystals were found. On examination these crystals proved to be a new mineral, having the composition $MgCO_3 + 3H_2O$. To this mineral, the authors have assigned the name of *nesquehonite*, after the locality where it was found, the Nesquehoning mine being one of the best known in Pennsylvania. The crystallisation of this mineral is orthorhombic. The authors also describe a crystallised artificial salt of the same composition as nesquehonite, obtained by dissolving magnesium carbonate in water containing carbonic anhydride, and allowing the solution to remain until crystals are deposited. Altered stalactites from the Nesquehoning mine were found to be pseudomorphs of nesquehonite after lansfordite, and from the crystal faces on the stalactites the authors have been able by very careful study to make out the crystallisation of the original lansfordite, a mineral at present only known as pseudomorphs. The crystals are triclinic, and the measurements given by the authors were obtained from 13 crystals. B. H. B.

Monazite from Ural. By C. W. BLOMSTRAND (*J. pr. Chem.* [2], **41**, 266—277).—The author has made fresh analyses of this mineral with a view of deciding whether the thorium which has been generally found therein is an essential constituent of the mineral, or is present merely as an accidental admixture of thorite. Three samples were analysed :—

I. Colour, light brown. Cleavage, easy. Powder, pale yellow. Sp. gr., 5·01. General formula, $100(3RO,P_2O_5) + 13(2RO,SiO_2) + 12H_2O$. Special formula, $20(Ce,La)_2(PO_4)_2 + 2ThSiO_4 + 0{\cdot}6R_2SiO_4 + 2{\cdot}4H_2O$.

II. Colour, dark yellowish-brown. Brittle. Fracture, splintering. Powder, pale yellow. Sp. gr., 5·266. Crystals, $2\frac{1}{2}$ cm. long, greatest thickness 1 cm., irregular. General formula, $100(3RO,P_2O_5) + 29(2RO,SiO_2) + 18H_2O$. Special formula, $20(Ce,La)_2(PO_4)_2 + Th_3(PO_4)_4 + 5{\cdot}4ThSiO_4 + R_2SiO_4 + 4H_2O$.

III. Small, indistinct crystals and crystalline fragments. Colour, faint greyish-brown. Cleavage not distinct. Sp. gr., 4·87. General formula, $100(3RO,P_2O_5) + 120(2RO,SiO_2) + 30H_2O$. Special formula, $20(Ce,La)_2(PO_4)_2 + 1{\cdot}2Th_3(PO_4)_4 + 7ThSiO_4 + 19R_2SiO_4 + 6H_2O$.

	P_2O_5.	SnO_2.	SiO_2.	ThO_2.	Ce_2O_3.	La_2O_3.	Y_2O_3.	Fe_2O_3.	FeO.
*I.	27·32	0·95	1·37	5·55	31·31	31·86	0·52	0·26	—
II.	25·09	0·43	2·90	17·82	34·90	17·60	0·43	0·43	—
III.	19·13	0·40	9·67	16·64	22·88	14·69	1·71	—	3·56

	Al_2O_3.	MnO.	CaO.	MgO.	H_2O.	Total.
*I.	0·13	—	0·55	—	0·41	100·23
II.	—	—	0·36	—	0·56	100·52
III.	2·90	4·89	1·25	0·40	0·71	98·83

A. G. B.

Minerals from Arizona. By W. P. BLAKE (*Amer. J. Sci.* [3], **39**, 43—45).—The sodium sulphate deposits of the Verde Valley, Arizona, have long been quarried as a substitute for salt for cattle. The occurrence of thenardite was made known by Silliman in 1881 (Abstr., 1881, 1109). A visit to the locality has enabled the author to describe allied species in association with the thenardite. The minerals described are mirabilite, halite, glauberite, and pseudomorphs of calcium carbonate after glauberite.

In conclusion, the author makes what he believes to be the first announcement of the occurrence of bournonite in the United States. It occurs sparingly in brilliant characteristic crystals at the Boggs mine, Big Bug district, Arizona. B. H. B.

Barium Sulphate from Perkins' Mill, Quebec. By E. S. DANA (*Amer. J. Sci.* [3], **39**, 61—65).—In 1889, Lacroix described (Abstr., 1889, 838), under the name of *michel-levite*, a mineral from Quebec, having the same composition as heavy spar, but, as he believed, crystallising in the monoclinic system. The discovery of the dimorphism of barium sulphate is a point of so great chemical interest that the author has been induced to examine upwards of 50 specimens from Perkins' Mill, Templeton, Quebec, the locality described by Lacroix. Optically and crystallographically, the specimens examined conform to normal barium sulphate. The apparent easy cleavage and the accompanying pearly lustres of one of the prismatic faces appear to be secondary in origin, and to have been called out by

* Mean of two analyses.

pressure. The existence of a monoclinic form of barium sulphate at Perkins' Mill is consequently extremely doubtful. B. H. B.

Jarosite from Utah. By F. A. GENTH (*Amer. J. Sci.* [3], **39**, 73). —At the Mammoth mine, Tintic district, Utah, minute crystals of jarosite occur, lining cavities of a siliceous limonite, and sometimes associated with a pulverulent yellow mineral, probably a basic ferric sulphate. The crystals are of a yellowish-brown colour, and exhibit rhombohedral forms. Analysis gave the following results:—

SiO_2.	Fe_2O_3.	Na_2O.	K_2O.	SO_3.	H_2O.	Sp. gr.
0·29	51·16	0·33	9·05	28·93	10·24	3·163

B. H. B.

Zinciferous Clays of South-west Missouri. By W. H. SEAMON (*Amer. J. Sci.* [3], **39**, 38—42).—In connection with the calamine deposits of Missouri, there occur, in considerable abundance, clays of peculiar composition, the probable commercial value of which has hitherto been unsuspected. They occur in layers of from several inches up to 3 feet, or in lumps weighing from 50 to 500 lbs., above, below, and intermixed with the calamine. The author gives 22 analyses, of which the following three are selected as typical:—

	H_2O.	Loss.	ZnO.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Total.	Sp. gr.
I.	4·03	3·92	54·06	35·29	1·64	—	1·80	100·74	2·91
II.	6·33	8·93	35·63	38·26	6·17	4·67	trace	99·99	2·77
III.	2·48	13·64	4·30	66·22	4·91	8·44	—	99·99	—

The loss at a low red heat consists mainly of water. I is a thin streak of a pure white variety of so-called "tallow clay" found in small amounts; II, flesh-coloured tallow clay from Aurora; III, dark red "joint clay" from Aurora. The clays termed joint clays by the miners are tougher than the tallow clay, and are usually found nearer the surface. B. H. B.

Composition of Recent Vesuvian Lavas. By G. FREDA (*Gazzetta*, **19**, 10—16).—*Lava of* 1884.—The surface of this lava is frequently coated with an extremely thin, hard, strongly adherent, bright, metallic film which contains iron and nitrogen, and gives off ammonia when boiled with concentrated potash solution, but differs from the ferric nitride observed by Silvestri, at Etna, by its permanence in the atmosphere.

Lava of 1886.—This is of a dark iron-grey colour, and contains crystals of augite and nodules of leucite disseminated throughout the interior. The surface, which is smooth, lustrous, and almost pitchy in appearance, is covered with a thin film which is seen to be yellow and transparent at the sharp angles. The powdered lava gelatinises when heated with dilute sulphuric acid. It fuses to a brown glass under the blowpipe.

Lava of 1887.—This lava resembles the preceding in appearance; but under the microscope it exhibits less ground-matrix. The nodules of leucite, which are of a dark-grey colour and contain numerous

inclusions, are less conspicuous; but the crystals of augite are more abundant than in the 1886 lava. The composition of these three lavas is as follows:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	P_2O_5.
Lava of 1884	48·06	18·37	10·62	9·46	3·51	5·63	1·80	0·69
„ 1886	48·56	17·91	11·93	8·94	3·68	6·21	1·65	0·77
„ 1887	48·40	18·09	10·81	9·53	3·45	5·48	2·13	0·62

S. B. A. A.

New Stone Meteorite. By L. G. Eakins (*Amer. J. Sci.* [3], **39**, 59—61).—The fragment of the meteorite described was presented by R. T. Hill to the United States National Museum. It is of irregular shape, and weighs $2\frac{1}{2}$ kilos. It is hard, compact, and very tough. The stony mass is very uniform in structure, but under the microscope is seen to consist of olivine and enstatite, with a small quantity of a colourless felspar. The mass has a sp. gr. of 3·543 at 30°, and on analysis yielded—

SiO_2.	Al_2O_3.	Cr_2O_3.	FeO.	Fe.	NiO.	Ni.	Co.	CaO.	MgO.
44·75	2·72	0·52	16·04	1·83	0·52	0·22	0·01	2·23	27·93

K_2O.	Na_2O.	P_2O_5.	S.	H_2O.	Total.	Less O for S.	Total.
0·13	1·13	0·41	1·83	0·84	101·11	0·92	100·19

The metallic portion constituted 2·23 per cent. of the mass and contained—

Fe.	Ni.	Co.	Total.
88·74	10·68	0·58	100·00

The residue from which the metallic portion had been removed was digested with dilute hydrochloric acid, and the soluble and insoluble portions analysed. In the soluble portion the ratio of the RO-group to the SiO_2 is very close to that of olivine. The insoluble portion, after removing the chromium oxide and a proportional amount of ferrous oxide to form chromite, gives ratios which seem to bear no definite relations to each other. Assuming, however, that the alumina and alkalis are present in the proportion required for a felspar of the oligoclase type, and deducting this amount of felspar, there remains—

$$RO : SiO_2 = 0·789 : 0·774,$$

which corresponds closely with enstatite. The general composition of the meteorite is as follows:—

Metallic.	Troïlite.	Soluble in acids.	Insoluble.	Total.
2·23	5·03	39·84	52·42	99·52

B. H. B.

Organic Chemistry.

Stereochemistry of Nitrogenous Compounds. By R. BEHREND (*Ber.*, 23, 454—458).—In the course of his researches on the alkyl-derivatives of hydroxylamine, made jointly with Leuchs and König, the author obtained results which appeared to show that whilst paranitrobenzylhydroxylamine and benzyl chloride on the one hand, and β-benzylhydroxylamine and nitrobenzyl chloride on the other, gave rise to the same β-benzylparanitrobenzylhydroxylamine, the hydrochlorides of the bases obtained by the two methods differed from one another in crystalline form and solubility. Further investigations have not confirmed this, but it has led the author to ideas concerning the nature of the nitrogen-atom which differ considerably from those of Hantzsch and Werner (this vol., p. 348).

The grounds on which the theory is based are as follows: Through the central points of the atoms, or groups of atoms combined with nitrogen in ammonia or the substituted ammonias, a plane may always be imagined to pass; whether this plane also passes through the centre of the nitrogen-atom is not discussed. Ammonia can unite simultaneously with a positive and negative element, and it is assumed that these take up their position on either side of the plane at points previously fixed; in other words, that ammonia has a positive and negative pole. This is graphically represented in Fig 1.

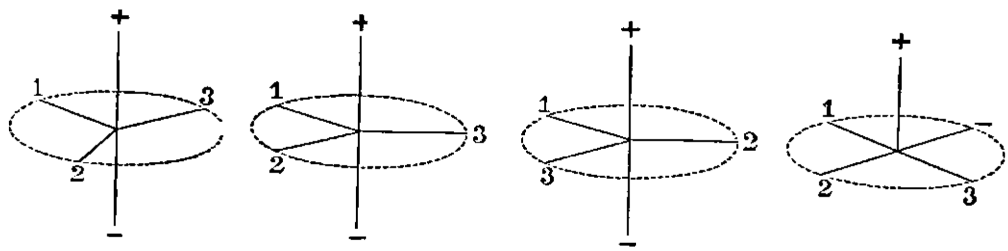
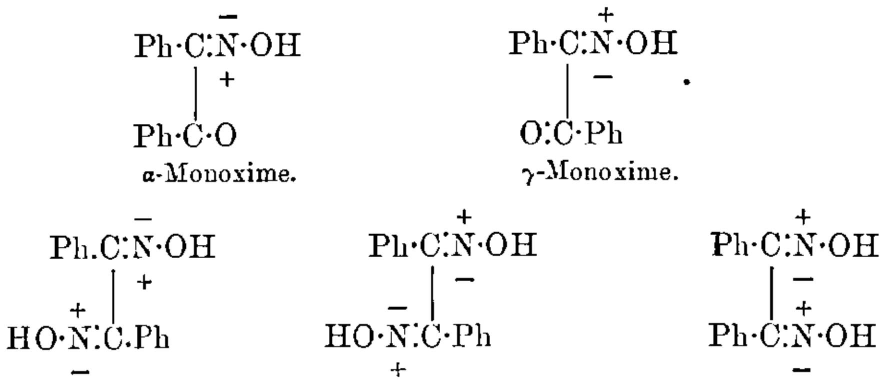


FIG. 1. FIG. 2. FIG. 3. FIG. 4.

If two different radicles (represented by 1 and 3) are substituted for two hydrogen-atoms in ammonia, two configurations are possible (Figs. 2 and 3), which would scarcely be distinguishable from one another, but whose salts would have the same relation to each other as the active tartaric acids. Experiments made to obtain such isomeric salts have so far been unsuccessful. It is, however, possible that as soon as both poles of the ammonia are saturated, the two isomerides may pass into the same state of equilibrium, as shown in Fig. 4. In favour of this view is the identity of the ammonium bases obtained on the one hand from diethylamine and methyl iodide, and on the other from dimethylamine and ethyl iodide (V. Meyer and Lecco, this Journal, 1876, i, 381).

The isomerism of the benzil monoximes and dioximes is explained by the assumption that the two carbon-atoms, which in themselves can, according to Van't Hoff and Wislicenus, rotate freely, take up

different positions of equilibrium under the influence of the attractions between the radicles with which they are combined. Whatever assumptions may be made as to the forces between these radicles, the monoxime can only exist in two, and the dioxime in three forms. If the phenyl-group be taken as feebly positive and the oxygen-atom as strongly negative, the following stereometric formulæ represent the compounds, the names given to each formula being only intended to indicate the one whose properties are best represented by that formula:—



α-Monoxime. γ-Monoxime.

α-Dioxime. β-Dioxime. γ-Dioxime.

This explanation is very closely allied to that previously given by V. Meyer and Auwers (Abstr., 1888, 597), and is in full accordance with the views of Wislicenus concerning the attraction which takes place between groups not directly connected together.

The author regards the above group of oximes as the only group of stereometric isomerides containing nitrogen which has been sufficiently investigated to allow of any conclusions as to the nature of the nitrogen-atom being drawn. He further doubts the validity of the proof given by Goldschmidt (this vol., p. 253), and adopted by Hantzsch and Werner (this vol., p. 248), as to the structural identity of the two benzaldoximes. The two forms of the latter which can, according to Behrend's theory, exist would show such slight differences as probably to be indistinguishable. H. G. C.

Arrangement in Space of the Atoms in Compounds containing Nitrogen. By C. W. Willgerodt (*J. pr. Chem.* [2], **41**, 291—300).—The author complains that Hantzsch and Werner (this vol., p. 348) have ignored his work on this subject (*J. pr. Chem.* [2], **37**, 449).

In this paper he gives figures showing the probable geometrical arrangement of several typical nitrogen compounds.

The author and F. Schulz have obtained two picryl-α-naphthylhydrazines: one forms yellow, almost pulverulent crystals; this is very unstable and, when treated with solvents or heated to 145—150°, easily changes into the other, a red-brown, stable modification; rotation of various parts of the molecule will probably explain such cases of isomerism.

The properties of the two hydrobenzoïns (Zincke, Abstr., 1880, 118) are easily explained on the supposition that they are geometrical

[illegible], $\begin{array}{l}OH\cdot CHPh \\ \quad\vert \\ OH\cdot CHPh\end{array}$ being the formula for isohydrobenzoïn, and $\begin{array}{l}OH\cdot CHPh \\ \quad\vert \\ \ H\cdot CPh\cdot OH\end{array}$ that for hydrobenzoïn.

A. G. B.

Preparation of Iodoform. By CASTHÉLAZ and BRUÈRE (*Chem. Centr.*, 1890, i, 19; from *Pharm. Zeit.*, **34**, 714).—By the method of Suilliot and Raynaud (Abstr., 1889, 1055), in which potassium hypoiodite reacts with acetone, the authors have obtained a very high yield of iodoform, the reaction occurring quantitatively between the hypoiodite and acetone. The iodoform thus prepared is completely soluble in alcohol, ether, chloroform, and carbon bisulphide, and has only a faint ethereal odour.

J. W. L.

Preparation of Octyl Chloride. By H. MALBOT (*Bull. Soc. Chim.* [3], **3**, 68—70; compare Abstr., 1889, 687).—Octyl alcohol, after saturation with hydrogen chloride and subsequent addition to the product of half its volume of concentrated hydrochloric acid, is heated in sealed vessels at 120—130°. The conversion is rapid, and the heating must not be prolonged. The yield is 87 per cent. of the theoretical.

T. G. N.

Action of Sulphur on Glycerol. By C. H. KEUTGEN (*Arch. Pharm.* [3], **28**, 1—7).—When sulphur and glycerol were heated together, there was no reaction below 285°; at 290° to 300° much gas was evolved with violent intumescence and partial coking of the mass. The gases consisted of hydrogen sulphide, carbonic anhydride, and ethylene. During the reaction, a distillate was obtained containing undecomposed glycerol, water, and sulphur, as well as a thick, oily, tenacious liquid. The receiver was provided with a condenser to prevent loss of allyl mercaptan. The distillate was treated with ether, which separated a pungent, fuming oil, found to be allyl mercaptan boiling at 90°. After distilling all ether from the residue, there were obtained, on cooling, crystals of sulphur and reddish-brown crystals of diallyl hexasulphide. The brown crystals were extracted by means of cold alcohol of 90 per cent., the alcohol evaporated, and this repeated until no more sulphur separated on cooling. The brown crystals have the empirical formula $C_3H_5S_3$, and when treated with nascent hydrogen from tin and hydrochloric acid, yield allyl sulphide and, in smaller quantity, allyl mercaptan. *Diallyl hexasulphide* forms reddish-brown, rhombic prisms which gradually darken in the air, and has a penetrating, repulsive odour; it melts at 75·5 and begins to volatilise at 180°, but with partial decomposition. It is very easily soluble in ether, less so in alcohol, and only in traces in water. With the alcoholic and ethereal solutions, water gives a yellow precipitate. Its alcoholic solution gives with mercuric chloride solution a yellow precipitate of $(C_3H_5)_2S_6,2HgCl_2$, and with platinum chloride solution, a reddish precipitate of $(C_3H_5)_2S_6,PtCl_4$.

Oxidation of the diallyl hexasulphide with nitric acid yielded an *oxysulphide*, $SO(C_3H_5)_2$, a yellow, thick, syrupy liquid, which becomes brown in the air, and at 0° forms an amorphous solid soluble in

alcohol and hot water. It is not volatile without decomposition. With nascent hydrogen, it yields allyl sulphide.

The first residue after removal of the diallyl hexasulphide formed a thick tenacious liquid which began to decompose at 110° with sudden increase of temperature and evolution of hydrogen sulphide, the mass coking even when heated in a vacuum. The residue thus obtained gave with nitric acid a mixture of oxalic and sulphuric acids.

J. T.

Benzoyl-derivatives of Carbohydrates, of Glucosamine, and of certain Glucosides. By L. KUENY (*Zeit. physiol. Chem.*, **14**, 330—371).—All carbohydrates on treatment with benzoic chloride, according to Baumann's method, give benzoyl compounds. On examining these compounds, they were found to be mixtures of higher and lower benzoylised substances; it was difficult, and in some cases impossible, to separate these, because few of them are crystalline, and their melting points are not well defined. Dilute solutions of carbohydrates give a mixture of benzoates with a higher percentage of carbon than concentrated solutions. With dextrose, the substances obtained in a fairly pure condition were the penta-, tetra-, and tri-benzoates melting respectively at 179°, 141°, and 80°. The other carbohydrates examined were levulose, saccharose, lactose, maltose, dextrin, and glycogen. Dextrose and galactose are, as Skraup (*Sitzungsb. Wien. Akbd. Naturw., Classe*, **98**, ii*b*, 438) first found, completely benzoylised; in the case of the other carbohydrates, one or more hydroxyl-groups are left unreplaced. All these compounds are very resistant to the action of dilute mineral acids; by treatment with fuming nitric acid, they are partially decomposed. On treatment with alkali, the benzoates of the glucoses show the greatest resistance, the benzoylised saccharoses come next, whilst the benzoyl-dextrins are easily saponified. Nearly all these compounds are very badly characterised, and were not obtained in a state of purity. Most of them have been previously obtained, but the derivatives of amylodextrin and erythrodextrin are new; these, however, in each case were only obtained as mixtures of several benzoates.

Baumann has shown that by treating glucosamine with benzoic chloride, a glucosamine tetrabenzoate is formed, mixed with lower benzoylised compounds; it was not possible to prepare a penta-benzoate. By the action of fuming nitric acid on the tetra-benzoate, a crystallisable dibenzoate melting at 166° was obtained. The sugar obtained from glucosamine is a reducing sugar, but is not fermentable with yeast. Its benzoyl compound comes in elementary composition nearest to a dextrose tribenzoate, but differs from that compound in being easily decomposed by acids and alkalis. Tetra-benzoylglucosamine gives no reaction with hydrocyanic acid and phenylhydrazine; it is not attacked by nitrous acid, from which it follows that one benzoyl-group is attached to the NH_2 residue. By treating the benzoyl compounds of glucosamine with sodium amalgam, there is no evolution of hydrogen; they thus resemble benzamide and hippuric acid, and therefore probably contain the group NHBz.

The glucosides, like the carbohydrates, are easily benzoylised on treating them according to Baumann's method. Of the four

glucosides examined, complete benzoylation, and a quite pure product (a pentabenzoate melting at 159—165°) was only obtained with one; namely, arbutin. Amygdalin, coniferin, and salicin were always incompletely benzoylised, giving mixtures of products containing a large number of benzoyl-groups, but these could not be separated by crystallisation. The benzoyl glucosides show even more resistance to the action of reagents than the similar compounds of the glucoses. Even by boiling with alkalis they were only decomposed with the greatest difficulty.
W. D. H.

Influence of Temperature on the Specific Rotation of Cane-sugar. By C. W. ANDREWS (*Chem. Centr.*, 1890, i, 20—21; from *Mon. Sci.* [4], **3**, 1366—1369).—The author has determined the specific rotation of cane-sugar, and his results coincide very closely with those of Dubrunfaut, who, in 1846, found that the rotation of cane-sugar diminishes as the temperature rises.

The author's determinations were made with a large Laurent polariscope, by means of which the angle of rotation could be read off to the nearest minute. The tubes, which were very carefully measured, were rather more than 40 cm. long. The sugar used was pure, and for a solution of the concentration C = 26·01 showed a rotation of 66·398° at 20°, whereas, according to Landolt's formula, it should be 66·421°. Two series of determinations were made. In the first, 100 c.c. contained 23·686 grams of sugar, the readings showing a specific rotation of $[\alpha]_D = 66·415°$ at 18·5° and $[\alpha]_D = 66·174°$ at 41·5°. In the second series, 100 c.c. contained 15·344 grams of sugar, with which the readings were equal to $[\alpha]_D = 66·642°$ at 19°, 66·405° at 39·9°, and 66·664° at 20·1°, from which results the author calculates $[\alpha]_D^t = [\alpha]_D^{20} - 0·000114\ (t - 20)$ for cane-sugar.
J. W. L.

Behaviour of the Hydroxides of Calcium and the Alkalis with Sugars. By H. LEPLAY (*Chem. Centr.*, 1890, i, 108—110; from *Zeit. Rüb. Zuck. Ind.*, 1889, 1017—1026).—After experimenting on the inversion of saccharose by water, the author made a similar series of experiments to determine the action of sodium and calcium hydroxides. A solution of sugar, containing 100 grams in 1 litre, was boiled with sodium hydroxide solution (strength, 50 alkaline degrees in 1 litre) for 52 hours. During the first 8 hours the alkali was found to have prevented the inversion, but from this time inversion begins, the polariscope readings being 97·2° at the commencement, 95·5° at the end of 12 hours, 93·1° at the end of 16 hours, 91·5° at the end of 20 hours, 75° at the end of 42 hours, 40·5° at the end of 54 hours. When heated without alkali, the same sugar solution became levorotatory at the end of 12 hours, and at the end of 54 hours the reading was − 21·5°. Two other similar experiments were made with a sugar solution of the same strength, but with considerably less alkali, from all of which the author concludes that the sodium hydroxide on the one hand prevents the inversion of the sugar, but that it attacks a portion of the sugar, becoming thereby itself neutralised. The rotatory power of the sugar solution is reduced, but the reducing power for Fehling's solution is not altered;

no reducing substances are formed if the heating be discontinued at the moment when the alkali is entirely neutralised. The action of calcium hydroxide on a similar solution of sugar proved to be the same as that of sodium hydroxide, but was more feeble ; a part of the alkali becomes neutralised, the rotatory power becomes reduced, but no reducing substance is formed. This coincides with the experiences of sugar refiners, an acid substance being formed which unites with the lime to form a thick syrupy liquid which prevents crystallisation. As the compound formed with sodium is of a much more limpid nature, the author recommends the use of sodium hydroxide.

The author draws attention to the importance of the estimation of these acid products of the decomposition of glucose, some of which reduce alkaline copper solutions, but do not rotate the ray of polarised light, and points out that whilst the quantity of glucose may remain nearly constant, the amount of these acids increases constantly, a small quantity of cane-sugar being continually converted into glueose, whilst at the same time a nearly corresponding quantity of glucose is converted into acid substances. J. W. L.

Compounds of Raffinose with Bases. By K. BEYTHIEN and B. TOLLENS (*Annalen*, **255**, 195—213; compare Abstr., 1889, 846). —The specific rotatory power of pure raffinose, $C_{18}H_{32}O_{16} + 5H_2O$, is $[\alpha]_D = 104·4°$.

Strontia raffinose, $C_{18}H_{32}O_{16},2SrO + H_2O$, is best prepared by boiling a solution of crystalline raffinose (5 grams), crystalline strontium hydrate (10 grams), and water (20 c.c.), for four to six hours in a salt-water-bath; at 100° the precipitate separates in a sticky condition, but by prolonged boiling in a salt-water-bath, or by adding a little alcohol, it is obtained as a granular, amorphous powder. It loses its water at 100°, and is soluble in alcohol and ether. Attempts to prepare a monostrontia compound were unsuccessful.

Baryta raffinose, $C_{18}H_{32}O_{16},BaO$, can be obtained by dissolving crystalline barium hydrate (2 grams) in water (60 c.c.), adding alcohol until the precipitate produced just redissolves, and then adding a solution of raffinose (2·5 grams) in water (5 c.c.). The reddish, amorphous precipitate gradually hardens, and is then washed with alcohol and ether. *Dibaryta raffinose*, $C_{18}H_{32}O_{16},2BaO$, is prepared in like manner, but employing excess (4—5 grams) of barium hydrate. Both compounds are difficult to purify.

Lime raffinose, $C_{18}H_{32}O_{16},3CaO + 2H_2O$, is easily obtained by dissolving raffinose (3 grams) in water (100 c.c.), adding calcium hydrate (0·4 gram), and, after keeping for some time, heating the filtered solution for some hours. It is a colourless powder, and loses its water at 100°.

Lead oxide raffinose, $C_{18}H_{32}O_{16},3PbO$, prepared by adding a clear ammoniacal solution of lead acetate to an aqueous solution of raffinose, is a colourless powder.

The two compounds $C_{18}H_{31}O_{16}Na$ and $C_{18}H_{31}O_{16}Na,NaOH$ were also prepared by the method previously described (Rischbieth and Tollens, (*Annalen*, **232**, 182). F. S. K.

Behaviour of Inverted Raffinose with Phenylhydrazine. By K. Beythien and B. Tollens (*Annalen*, **255**, 214—216).—When raffinose (10 grams) is heated for ten minutes at 68° with hydrochloric acid of sp. gr. 1·19 (6 c.c.) and water (90 c.c.), the solution then freed from hydrochloric acid with silver carbonate, and treated with phenylhydrazine and acetic acid, an osazone is obtained which has the same melting point and the same composition as the osazone of levulose and of dextrose. This experiment, together with Haedicke and Tollens' observation that the glucose formed is strongly lævorotatory, proves that levulose is produced by the partial inversion of raffinose. The fact that galactose cannot be isolated from the inverted solution, in spite of the readiness with which it crystallises, seems to show the existence of a compound of galactose with dextrose in the partially inverted solution.

Mannose phenylhydrazine could not be obtained from the inverted solution, as stated by Fischer (Abstr., 1889, 480). F. S. K.

Cellulose and its Forms. By W. Hoffmeister (*Chem. Centr.*, 1890, i, 112—114; from *Landw. Jahrb.*, **18**, 767—784).—The author has further experimented with the two methods already described (*Chem. Centr.*, 1888, 1211, 1426; 1889, ii, 721). Although cellulose may be purified by treatment with cold hydrochloric acid and hot ammonia, which remove the foreign substances, after which the cellulose is completely dissolved by cuprammonium hydroxide solution, it is now recommended to use glacial acetic acid, which does not effect any change in any form of soluble cellulose in the cold, sugar-formation not occurring until a few degrees below 100°. Starch is not affected by acetic acid at 88—92°, but if one drop of hydrochloric acid is added, the starch becomes completely dissolved in 2 to 3 hours. Substances are therefore digested for several hours at 86—90° with 5 parts of glacial acetic acid, to which one drop of hydrochloric acid per 20 c.c. is added, after which the residue is digested with ammonia and thoroughly washed, and may then be dissolved in cuprammonium hydroxide solution. The method is, however, too complicated for the usual determination of cellulose in feeding stuffs.

The "chlorine mixture" is useful for the approximate determination of crude woody fibre, and for the preparation of the soluble and insoluble forms of cellulose, but is not suitable for the analysis of feeding stuffs.

The author considers that Weender's method is the best for this purpose. He has also made a series of experiments with clover and barley, with the object of determining whether soluble forms of cellulose occur at every period of the life of plants, and whether the relative proportions of soluble and insoluble cellulose can be determined during the different periods of plant life, and he has arrived at the conclusion that soluble cellulose does exist at every period of the life of plants, and that the relative proportion of soluble cellulose increases with the period of vegetation. J. W. L.

The Melting Points and Preparation of Osazones. By K. Beythien and B. Tollens (*Annalen*, **255**, 217—221).—The observed

melting point of an osazone depends, as has been previously stated by other investigators, on the rapidity of heating; the levulosazone obtained from raffinose, for example, melts at 208° when the rise in temperature from 23—208° occurs in 13 minutes, whilst by heating much more slowly the melting point falls to 185°. It is advisable, therefore, in identifying an osazone by its melting point, to do so by direct comparison.

In the preparation of osazones from phenylhydrazine acetate (or phenylhydrazine hydrochloride and sodium acetate), the solution should not be evaporated to dryness, as, under these conditions, acetylphenylhydrazine (m. p. 128·5°) is also formed.

Phenylhydrazine, under certain conditions not determined, produces troublesome sores on the skin. F. S. K.

Ethyl Orthoformate. By T. HULLEMAN (*Rec. Trav. Chim.*, **8**, 386—390).—It is stated in text-books that ethyl orthoformate is decomposed by sodium ethoxide; alcohol, ether, sodium formate, and carbonic monoxide being formed. The author finds that this is not the case. Ethyl orthoformate is not acted on by a 10 per cent. alcoholic solution of sodium ethoxide at 100°, nor by dry sodium ethoxide at 146°; when boiled with metallic sodium, a small quantity of a brown substance is formed, but no gas is evolved.

Nitric acid decomposes ethyl orthoformate, forming ethyl nitrate, formic acid, and water; a small quantity of ordinary ethyl formate is also formed. C. F. B.

Ethyl Thioacetoacetate. By A. MICHAELIS and B. PHILIPS (*Ber.*, **23**, 559—561).—Ethyl thioacetoacetate (m. p. 100—101°) is formed when ethyl acetoacetate is treated with thionyl chloride in the cold.

When ethyl thioacetoacetate is treated with phenylhydrazine in cold acetic acid solution, it yields a compound of the composition $C_{20}H_{22}O_4N_2S$. This substance separates from hot alcohol in colourless crystals, melts at 185°, and is converted into phenylmethylpyrazoloneazobenzene, identical with the compound described by Buchka and Sprague (this vol., p. 28), when it is warmed with phenylhydrazine in alcoholic solution. F. S. K.

Formation of Lactic Acid from Raffinose and from Cane-sugar. Raffinose not formed from Cane-sugar by the Action of Calcium or Strontium Hydroxide. By K. BEYTHIEN, E. PARCUS, and B. TOLLENS (*Annalen*, **255**, 222—228).—Lactic acid (0·6 gram) is formed when raffinose (40 grams) is boiled for about 24 hours with a solution of crystalline strontium hydroxide (90 grams) in water (1 litre). Cane-sugar under the same conditions gives the same quantity of lactic acid.

When cane-sugar (1 part) is boiled with calcium hydroxide (1 part) and water (20 parts) for 48 hours, it yields about 1 per cent. of its weight of lactic acid; raffinose is not formed when cane-sugar is boiled with calcium or strontium hydroxide, as is shown by the fact that after separating the alkaline earth and oxidising the residual sugar with nitric acid, not a trace of mucic acid is obtained.

F. S. K.

Lactic Acid from Molasses. By K. Beythien, E. Parcus, and B. Tollens (*Annalen*, **255**, 228—229).—Molasses contains variable quantities of lactic acid, sometimes as much as 0·5 per cent. The authors examined four different samples and found lactic acid in every case; two of the samples were obtained from works where the elution process and the strontia process are not employed.

F. S. K.

New Synthesis of Bibasic Carbon Acids. By A. Crum Brown (*Proc. Roy. Soc. Edin.*, **17**, 53—54).—The electrolysis of salts of the general formula COOK·R″·COOEt has produced potassium hydroxide, hydrogen, and carbonic anhydride at the cathode, and salts of the formula COOEt·R·R·COOEt at the anode. See next abstract.

E. W. P.

Electrolysis of Potassium Ethyl Malonate and of Potassium Ethyl Succinate. By A. Crum Brown and J. Walker (*Proc. Roy. Soc. Edin.*, **17**, 54—56).—Avoiding heating and high concentration, potassium ethyl malonate was subjected to electrolysis; and after the passage of the current for some time, potassium carbonate was deposited, and from the aqueous solution ether extracted ethyl succinate (b. p. 216°).

Ethyl adipate was obtained in a similar manner from potassium ethyl succinate.

E. W. P.

Lactonic Acids, Lactones, and Unsaturated Acids. By R. Fittig (*Annalen*, **255**, 1—18; compare Abstr., 1886, 47, and 1888, 251).—The condensation of aldehydes with dicarboxylic acids of the succinic series is a reaction which can be employed with advantage for the preparation of lactonic acids, lactones, and unsaturated mono- and di-carboxylic acids, the constitution of which is known from their method of formation.

All aldehydes hitherto investigated in this direction react readily with succinic acid and with pyrotartaric acid; other dicarboxylic acids have not yet been tried.

The usual method of procedure is to heat an intimate mixture of the anhydrous aldehyde (1 mol.), anhydrous sodium succinate (1 mol.) or sodium pyrotartrate (1 mol.), and freshly distilled acetic anhydride (1 mol.), at a temperature varying from 80 to 120°.

In the case of succinic acid, the first product is probably a sodium salt of the constitution $OH{\cdot}CHR{\cdot}CH(COONa){\cdot}CH_2{\cdot}COONa$; this compound, on treatment with water, is decomposed by the acetic acid into the free acid or the sodium hydrogen salt, with subsequent formation of a single lactonic acid. The yield of this product is only approximately quantitative, owing to the formation of resinous products, especially when the aldehyde employed is prone to polymerisation.

In the case of pyrotartaric acid, two isomeric lactonic acids of the constitution $\begin{array}{l} CHR{\cdot}CH{\cdot}COOH \\ \;| \qquad\;\; | \\ O{\cdot}CO{\cdot}CHMe \end{array}$ and $\begin{array}{l} CHR{\cdot}CMe{\cdot}COOH \\ \;| \qquad\;\; | \\ O{\cdot}CO{\cdot}CH_2 \end{array}$, respectively, are formed; the acid of higher melting point is produced in by far

the larger quantity, and has probably the constitution represented by the first of the two formulæ.

Salicylaldehyde and succinic acid yield a *dicoumarin* of the constitution $C_6H_4<\genfrac{}{}{0pt}{}{O\cdot CO}{-\ CH}>C\cdot C<\genfrac{}{}{0pt}{}{CO\cdot O}{CH\ -}>C_6H_4$, whilst salicylaldehyde and pyrotartaric acid give *coumarinpropionic acid*,

$$C_6H_4<\genfrac{}{}{0pt}{}{O\cdot CO}{-CH}>C\cdot CHMe\cdot COOH,$$

and small quantities of a *hydroxyphenylmethylisocrotonic acid*, which has probably the constitution $OH\cdot C_6H_4\cdot CH\colon CMe\cdot CH_2\cdot COOH$.

Anisaldehyde and succinic acid condense together, forming *anisylisocrotonic acid*, $OMe\cdot C_6H_4\cdot CH\colon CH\cdot CH_2\cdot COOH$, *dianisylpentolic acid*, $OMe\cdot C_6H_4\cdot CH\colon CH\cdot C(COOH)\colon CH\cdot C_6H_4\cdot OMe$, and *dianisyltetrylene*, $OMe\cdot C_6H_4\cdot CH\colon CH\cdot CH\colon CH\cdot C_6H_4\cdot OMe$.

The distillation-products of the monosubstituted paraconic acids are in every case (1) a monocarboxylic $\beta\gamma$-unsaturated acid formed by the elimination of carbonic anhydride; (2) small quantities of a saturated lactone isomeric with this $\beta\gamma$-acid; and (3) one, or in the case of methylparaconic acid several, unsaturated dicarboxylic acids isomeric with the original paraconic acid; in every case, except in that of phenylparaconic acid, some of the acid passes over unchanged, especially with rapid distillation.

The lactonic acids obtained from aldehydes and pyrotartaric acid yield, on distillation, unsaturated hydrocarbons; only very small quantities of unsaturated monocarboxylic acids and lactones being produced; at the same time, some of the lactonic acid is decomposed into pyrotartaric acid and the aldehyde from which it was prepared.

F. S. K.

Acetaldehyde and Succinic Acid. By R. FITTIG and I. FRÄNKEL (*Annalen*, **255**, 18—42; compare Abstr., 1886, 47, 1888, 251).—*Methylparaconic acid*, $\begin{array}{l}CHMe\cdot CH\cdot COOH\\ |\qquad\quad\ \ |\\ O\cdot CO\cdot CH_2\end{array}$, is obtained when a mixture of sodium succinate, acetic anhydride, and acetaldehyde ($1\frac{1}{2}$ mols.) is heated for 12 hours at 100°, and then for 24 hours at 115—120°. The product is mixed with water, the supernatant oil, which consists of paraldehyde and resinous products, separated mechanically, the residual solution distilled with steam to free it from aldehyde, and then concentrated by evaporation; after acidifying with hydrochloric acid, the methylparaconic acid and succinic acid are extracted with ether, dissolved in water, the filtered solution evaporated to dryness, and the lactonic acid extracted with chloroform. It crystallises from benzene in slender needles or plates, melts at 83—84°, and is very readily soluble in most ordinary solvents, but only sparingly in benzene and light petroleum, and almost insoluble in carbon bisulphide. This acid seems to have been previously prepared by Gantter (compare Bischoff and Rach, Abstr., 1886, 1012) by the reduction of ethyl acetosuccinate with sodium amalgam. The *barium* salt, $(C_6H_7O_4)_2Ba + 3\frac{1}{2}H_2O$, prepared by neutralising a cold aqueous solution of the acid with barium carbonate, is very readily soluble in water, from which it separates in small needles; it loses its water at 100°, and is

insoluble in alcohol. The *calcium* salt ($+ 2\frac{1}{2}H_2O$) separates from very concentrated aqueous solutions in ill-defined, crystalline aggregates. The *silver* salt, $C_6H_7O_4Ag$, crystallises in prisms, is very stable, and dissolves freely in hot water.

Barium methylitamalate, $C_6H_8O_5Ba + 3H_2O$, is produced when methylparaconic acid is boiled with baryta-water; it is not easily obtained in crystals. The *calcium* salt ($+ 3H_2O$), prepared in like manner, crystallises from water in small needles, and is more readily soluble in cold than in hot water. The *silver* salt, $C_6H_8O_5Ag_2$, is a colourless, flocculent compound, only sparingly soluble in water.

When methylparaconic acid is heated, carbonic anhydride commences to be evolved at 200°, and at a somewhat higher temperature, a yellow oil distils, leaving a small quantity of carbonaceous matter. The distillate is a mixture of valerolactone, ethylidenepropionic acid, methylitaconic acid, methylcitraconic acid, and unchanged methylparaconic acid; the five compounds are isolated as follows:—The distillate is treated with water, rendered alkaline with sodium carbonate, and the valerolactone extracted with ether; the solution is then acidified with sulphuric acid, the acids extracted with ether, and the mixture submitted to distillation with steam. Methylitaconic acid and methylparaconic acid remain, and can be separated by evaporating the solution and extracting the lactonic acid from the crystalline residue with chloroform. Ethylidenepropionic acid and methylcitraconic acid distil over, and can be separated by converting them into the barium salts and evaporating, whereon the sparingly soluble salt of methylcitraconic acid separates from the hot solution.

Ethylidenepropionic acid, $CH_3{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH$, is a colourless oil boiling at 193—194°; it is soluble in 10—12 parts of water, but separates from the solution on the addition of sodium chloride. It is moderately easily volatile with steam, and has an odour recalling that of hydrosorbic acid. This acid is possibly identical with the compound obtained by Zincke and Küster (Abstr., 1889, 599) from catechol and orthamidophenol, and named by them propylideneacetic acid. The *barium* salt, $(C_5H_7O_2)_2Ba$, separates from water in small, anhydrous needles, and is more sparingly soluble in hot than in cold water. The *calcium* salt ($+ H_2O$) crystallises in plates, and is readily soluble in water and alcohol. The *silver* salt, $C_5H_7O_2Ag$, crystallises from water in nacreous plates, and is slowly decomposed by boiling water, but is moderately stable in the light.

γ-Bromovaleric acid, $CH_3{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is obtained when ethylidenepropionic acid is treated with ice-cold concentrated hydrobromic acid. It is a colourless oil, and is readily decomposed by boiling water, yielding valerolactone.

Dibromovaleric acid, $CH_3{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2{\cdot}COOH$, prepared by brominating ethylidenepropionic acid in cold carbon bisulphide solution, is a thick, yellowish syrup; it is not identical with the dibromo-derivative of allylacetic acid.

Methylcitraconic acid, $COOH{\cdot}CH{:}CEt{\cdot}COOH$, crystallises from water and chloroform in large, compact prisms, and from benzene in needles, melts at 100—101°, and is readily volatile with steam; it probably distils as anhydride, because even when dried at 70° it is

converted into the anhydride, which remains as an oil. The *calcium* salt, $C_6H_6O_4 + H_2O$, separates from hot water in plates, and is more readily soluble in cold than in hot water. The *barium* salt ($+ 4H_2O$) separates from its aqueous solutions, on heating, in slender needles, and loses its water only at a high temperature. The *silver* salt, $C_6H_6O_4Ag_2$, crystallises from hot water, in which it is only very sparingly soluble, in colourless needles, and is very stable.

Methylitaconic acid, COOH·CH$_2$·C(COOH):CHMe, crystallises from hot water in prisms, melts at 166—167°, and is only sparingly soluble in cold ether and cold water, and almost insoluble in chloroform. It is not volatile with steam, and is much more sparingly soluble than methylcitraconic acid, to which it stands in the same relation as itaconic does to citraconic acid. The *calcium* salt, $C_6H_6O_4Ca + H_2O$, crystallises from water in plates, and is more readily soluble in cold than in hot water. The *barium* salt ($+ \frac{1}{2}H_2O$) separates from water in prismatic crystals. The *silver* salt, $C_6H_6O_4Ag_2$, is a crystalline powder, very sparingly soluble in water, and very stable.

Methylcitraconic acid is converted into methylitaconic acid when it is heated with water at 150° for 6—8 hours; when methylitaconic acid is distilled, it is partially converted into methylcitraconic acid. Methylitaconic acid and methylcitraconic acid, on reduction with sodium amalgam, are both converted into ethylsuccinic acid (m. p. 98—99°) identical with the compound obtained by Huggenberg (Abstr., 1878, 782).

An acid melting at 194—196°, and sparingly soluble in hot water, is formed when methylcitraconic acid is heated with dilute (1 : 4) nitric acid; this compound is probably methylmesaconic acid.

F. S. K.

Chloral and Succinic Acid. By R. FITTIG and H. E. MILLER (*Annalen*, **255**, 43—55; compare Abstr., 1888, 252).—Trichloromethylparaconic acid is prepared by treating chloral with sodium succinate and acetic anhydride, and, as soon as the first energetic reaction is at an end, heating the mixture at 110—120° for three to four hours. The product is mixed with warm water, the filtered solution strongly acidified with sulphuric acid, extracted with ether, and the ether evaporated; the acid is then purified by repeatedly dissolving in water and evaporating the filtered solution, and finally it is dissolved in chloroform to free it from traces of succinic acid. The yield of the pure acid is about 60 per cent. of the theoretical quantity. It crystallises in slender needles, melts at 97°, and is very readily soluble in ether, alcohol, and chloroform, but less readily in warm benzene, and almost insoluble in carbon bisulphide. The *calcium* salt, $(C_6H_4Cl_3O_4)_2Ca + 2H_2O$, prepared by neutralising a cold aqueous solution of the acid with calcium carbonate, crystallises in prisms. The *barium* salt, $(C_6H_4Cl_3O_4)_2Ba$, is a colourless, crystalline, hygroscopic compound. The *silver* salt, $C_6H_4Cl_3O_4Ag$, crystallises from hot water in slender needles.

Calcium trichloritamalate, $C_6H_5Cl_3O_5Ca$, separates as a colourless powder when a neutral solution of calcium trichloromethylparaconate is evaporated on the water-bath; the *barium* salt cannot be obtained in this way.

When a solution of trichloromethylparaconic acid is boiled with bases, salts of isocitric acid are formed.

Isocitric acid (*loc. cit.*) is obtained by boiling the paraconic acid with baryta. The barium salt, which separates on prolonged boiling as an insoluble, amorphous powder, is extracted with boiling water until free from chlorine, decomposed with boiling acetic acid, the barium precipitated with sulphuric acid, and the filtrate repeatedly evaporated with water. The residue solidifies, after some weeks, to a yellowish, very hygroscopic mass which consists of a mixture of isocitric acid and $\beta\gamma$-butyrolactonedicarboxylic acid. Salts of isocitric acid can be prepared from this mixture by neutralising the aqueous solution with a carbonate in the cold, and purifying the salt by repeatedly dissolving it in water and reprecipitating with alcohol. The *calcium* salt, $(C_6H_5O_7)_2Ca_3 + H_2O$, is a colourless, amorphous compound, sparingly soluble in hot water. The *barium* salt ($+ H_2O$) is more sparingly soluble than the calcium salt. The silver salt, $C_6H_5O_7Ag_3$, is a light-brown, amorphous powder.

Lactoisocitric acid (*$\beta\gamma$-butyrolactonedicarboxylic acid*),

$$CO<\begin{matrix}O - CH\cdot COOH \\ CH_2\cdot CH\cdot COOH\end{matrix},$$

is formed when isocitric acid is kept over sulphuric acid under reduced pressure, or heated at 100°. The *calcium* salt, $C_6H_4O_6Ca + 3H_2O$, prepared by neutralising a cold, aqueous solution of the acid with calcium carbonate, crystallises in colourless needles, and is sparingly soluble in cold, but more readily in hot water. The *barium* salt, $C_6H_4O_6Ba$, and the *silver* salt, $C_6H_4O_6Ag_2$, are amorphous.

Dichloromethylparaconic acid, $CO<\begin{matrix}O - CH\cdot CHCl_2 \\ CH_2\cdot CH\cdot COOH\end{matrix}$, is obtained when the trichlorinated acid is dissolved in glacial acetic acid, and zinc-dust gradually added to the warm solution. It crystallises from water in prisms, melts at 142°, and is soluble in ether and alcohol, but only sparingly in cold chloroform and benzene, and is almost insoluble in light petroleum. When boiled with baryta, it yields a colourless compound melting at about 222°, which still contains chlorine; this substance is being investigated.

When trichloromethylparaconic acid is distilled, about one-third passes over unchanged, the remainder being completely decomposed.

F. S. K.

Propaldehyde and Succinic Acid. By R. Fittig and A. Delisle (*Annalen*, **255**, 56—68).—Ethylparaconic acid, $\begin{matrix}CHEt\cdot CH\cdot COOH \\ O\cdot CO\cdot CH_2\end{matrix}$, is obtained by heating a mixture of propaldehyde, sodium succinate, and acetic anhydride for 25—30 hours at 110—120° (compare Abstr., 1886, 47). The product is distilled with water to free it from neutral oils, the filtered solution strongly acidified and extracted with ether; on evaporating the ether, there remains a mixture of ethylparaconic acid and succinic acid, from which the lactonic acid is extracted with chloroform. It crystallises from water in needles,

melts at 85°, and is very readily soluble in chloroform, ether, and water, but only moderately easily in light petroleum, and almost insoluble in carbon bisulphide. The *silver* salt, $C_7H_9O_4Ag$, crystallises from boiling water in needles. The *calcium* salt, $(C_7H_9O_4)_2Ca + 2H_2O$, prepared by neutralising an aqueous solution of the acid with calcium carbonate in the cold, crystallises in needles, and is readily soluble in water. The *barium* salt $(+3H_2O)$ crystallises in well-defined prisms.

Calcium ethylitamalate, $C_7H_{10}O_5Ca + 5H_2O$, is obtained by boiling ethylparaconic acid with lime-water; it crystallises in needles, and is insoluble in alcohol, and more sparingly soluble in hot than in cold water. The *barium* salt $(+3H_2O)$ resembles the calcium salt, and is more sparingly soluble in hot than in cold water. The *silver* salt, $C_7H_{10}O_5Ag_2$, is amorphous.

Ethylparaconic acid is decomposed when heated, with evolution of carbonic anhydride, and between 200° and 300° almost the whole distils, the distillate consisting of caprolactone, hydrosorbic acid, $C_6H_{10}O_2$ (b. p. 208°), and unchanged ethylparaconic acid.

F. S. K.

Butaldehyde and Succinic Acid. By R. Fittig and H. Schmidt (*Annalen*, **255**, 68—86).—*Propylparaconic acid*, $\begin{matrix} CHPr\cdot CH\cdot COOH \\ | \quad\quad | \quad\quad\quad \\ O\cdot CO\cdot CH_2 \quad\quad \end{matrix}$, is prepared by heating a mixture of normal butaldehyde, acetic anhydride, and sodium succinate at 100° for 12 hours, and then for 24 hours at 120—125°, and purifying the product as described in the case of ethylparaconic acid (compare preceding abstract). The yield is 45 to 50 per cent. of the aldehyde employed. It crystallises in waxy plates, melts at 73·5°, and is readily soluble in chloroform and hot water, but only very sparingly in light petroleum, and insoluble in carbon bisulphide. The *calcium* salt, $(C_8H_{11}O_4)_2Ca + 2H_2O$, prepared in the usual manner, separates from cold water in crystalline crusts. The *barium* salt, $(C_8H_{11}O_4)_2Ba$, is a colourless, amorphous powder, readily soluble in water. The *silver* salt, $C_8H_{11}O_4Ag$, crystallises in long needles, is soluble in water, and is very stable.

Calcium propylitamalate, $C_8H_{12}O_5Ca + 5H_2O$, prepared by boiling the paraconic acid with lime-water, crystallises from water in moss-like needles, and is more readily soluble in cold than in hot water. The *barium* salt $(+2H_2O)$ forms crystalline scales, and resembles the calcium salt in properties. The *silver* salt, $C_8H_{12}O_5Ag_2$, is almost insoluble in hot water and rather sensitive to light.

When propylparaconic acid is heated, carbonic anhydride is evolved, and at 230—240° a yellow oil distils; this distillate consists principally of heptylenic acid, but contains also small quantities of propylitaconic acid (or its anhydride) and heptolactone, together with variable quantities of unchanged paraconic acid. After isolating the lactone in the usual manner, the residual alkaline solution is acidified and the heptylenic acid distilled with steam; the residue contains propylitaconic acid and propylparaconic acid, which can be isolated by extracting with ether, and separated by means of chloroform, in which the lactonic acid alone is readily soluble.

Heptylenic acid, CHPr:CH·CH_2·COOH (Abstr., 1888, 251), has the peculiar odour of unsaturated acids, and is rather sparingly soluble in water. The *barium* salt, $(C_7H_{11}O_2)_2Ba$, crystallises from hot water in plates. The *calcium* salt ($+H_2O$) is rather more soluble in cold than in hot water, crystallises in plates, and is readily soluble in alcohol. The *silver* salt, $C_7H_{11}O_2Ag$, separates from boiling water, in which it is readily soluble, in small needles, but considerable decomposition occurs.

γ-Bromoheptylic acid, CHPrBr·CH_2·CH_2·COOH, prepared by dissolving heptylenic acid in cold hydrobromic acid, and keeping the solution for several days in the cold, is a thick, heavy oil; it is slowly decomposed by water at the ordinary temperature yielding heptolactone.

Heptolactone (γ-propylbutyrolactone) boils at 234·5—235·5° without decomposition (compare Abstr., 1888, 252).

Barium hydroxyheptylate, $(C_7H_{13}O_3)_2Ba$, prepared by boiling heptolactone with baryta, crystallises from hot alcohol in microscopic needles which deliquesce on exposure to the air. It is decomposed when heated at 100° or when boiled with water, the odour of heptolactone being perceptible. The *silver* salt, $C_7H_{13}O_3Ag$, is partially decomposed by boiling water, from which it separates in moss-like crystals; it quickly darkens on exposure to the light.

Hydroxyheptylic acid can be obtained by decomposing a well-cooled solution of the barium salt with 1 per cent. hydrochloric acid, extracting with ether, and evaporating the ethereal solution at 0°; it is a strongly acid syrup, soluble in water, but it very readily changes into the lactone.

Propylitaconic acid, COOH·CH_2·C(COOH):CHPr, crystallises from hot water and ether in prisms, melts at 159°, and is decomposed at about 200—210°, being probably converted into the anhydride. It is almost insoluble in chloroform and carbon bisulphide, and only sparingly soluble in cold water and benzene, but readily in ether, alcohol, and hot water. The *barium* salt, $C_8H_{10}O_4Ba$, contains water of crystallisation, and is more readily soluble in cold than in hot water.

F. S. K.

Isobutaldehyde and Succinic Acid. By R. FITTIG and A. ZANNER (*Annalen*, **255**, 86—96; compare Abstr., 1886, 47, 1888, 251). —*Isopropylparaconic acid*, $\begin{matrix}\text{CHPr}^{\beta}\cdot\text{CH}\cdot\text{COOH}\\ | \qquad\quad |\qquad\\ \text{O—CO}\cdot\text{CH}_2\qquad\end{matrix}$, is obtained by heating a mixture of isobutaldehyde, sodium succinate, and acetic anhydride at 110—120° for 40 hours. The acid is isolated as described in the case of ethylparaconic acid. It crystallises from boiling benzene in colourless plates, melts at 68—69°, and is readily soluble in water, ether, and chloroform, but only sparingly in carbon bisulphide, and insoluble in light petroleum. The *barium* salt, $(C_8H_{11}O_4)_2Ba + 3H_2O$, prepared by treating an aqueous solution of the acid with barium carbonate in the cold, crystallises in colourless plates. The *calcium* salt ($+2H_2O$) crystallises in needles, and is readily soluble in water. The *silver* salt, $C_8H_{11}O_4Ag$, crystallises from boiling water in colourless needles, and does not darken on exposure to light.

Barium isopropylitamalate, $C_8H_{12}O_5Ba + 2H_2O$, is formed when the paraconic acid is boiled with baryta-water; it crystallises in small needles, and is more readily soluble in cold than in hot water. The *silver* salt, $C_8H_{12}O_5Ag_2$, is crystalline, almost insoluble in boiling water, and moderately sensitive to light.

When isopropylparaconic acid is distilled, isoheptolactone (dimethylvalerolactone) and isoheptylenic acid are formed with evolution of carbonic anhydride, whilst some of the acid passes over unchanged; the products can be separated in the usual manner (compare preceding abstract).

Isoheptylenic acid, $CHPr^{\beta}{:}CH{\cdot}CH_2{\cdot}COOH$, is a colourless oil, boils at 217° (thermometer entirely in vapour), and is volatile with steam; it is specifically lighter than and only sparingly (1 in 110) soluble in cold water, but it is much more readily soluble in hot water. The *barium* salt, $(C_7H_{11}O_2)_2Ba$, prepared in the cold, crystallises in anhydrous needles. The *calcium* salt ($+ 1\frac{1}{2}H_2O$) crystallises in transparent prisms. The *silver* salt, $C_7H_{11}O_2Ag$, crystallises from boiling water in slender needles, darkens on exposure to light, and decomposes at 100°.

γ-Bromoisoheptylic acid, $CHPr^{\beta}Br{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is formed when the preceding compound is treated with concentrated hydrobromic acid in the cold, but it cannot be obtained in a pure condition.

Isoheptolactone (*dimethylvalerolactone*), $CHPr^{\beta}{<}\begin{matrix}CH_2{\cdot}CH_2\\ O\text{—}CO\end{matrix}$, is formed when bromoisoheptylic acid is boiled with water, but it is more easily prepared by warming isoheptylenic acid with dilute (1 : 1) sulphuric acid. It is a colourless oil, boils at 224—225° (uncorr.), and is readily volatile with steam; it dissolves in about 35 parts of cold water, the solution becoming turbid on heating, and then clear again at a higher temperature.

Barium hydroxyisoheptylate, $(C_7H_{13}O_3)_2Ba$, is obtained when the lactone is boiled with baryta-water. The *silver* salt, $C_7H_{13}O_3Ag$, is only sparingly soluble in water. The free acid seems to be less stable than γ-hydroxyheptylic acid.

F. S. K.

Valeraldehyde and Succinic Acid. By R. Fittig and A. Schneegans (*Annalen*, **255**, 97—108; compare Abstr., 1886, 47, 1888, 251).—*Isobutylparaconic acid*, $CO{<}\begin{matrix}O\text{—}CH{\cdot}CH_2Pr^{\beta}\\ CH_2{\cdot}CH{\cdot}COOH\end{matrix}$, is prepared by heating a mixture of valeraldehyde, acetic anhydride, and sodium succinate at 110° for 18 to 20 hours. The product is mixed with water, the separated oil extracted with ether and treated with sodium carbonate; unchanged valeraldehyde and condensation-products remain undissolved, whilst the lactonic acid passes into solution and is reprecipitated on the addition of acid. Some of the lactonic acid and unchanged succinic acid remain as sodium salts in the original acetic acid solution; after strongly acidifying with hydrochloric acid and extracting with ether, the two compounds are separated by treatment with chloroform. Isobutylparaconic acid crystallises from cold water in small needles, melts at 124—125°, and sublimes, when

carefully heated, in colourless plates. It is readily soluble in alcohol, ether, chloroform, and light petroleum. The *silver* salt, $C_9H_{13}O_4Ag$, is very stable and soluble in hot water. The *calcium* salt, $(C_9H_{13}O_4)_2Ca + 2H_2O$, crystallises in small needles, and is soluble in alcohol and hot water. The *barium* salt ($+3H_2O$) crystallises in small, well-defined, rhombic prisms, and is readily soluble in alcohol. The *zinc* salt ($+1\frac{1}{2}H_2O$) crystallises in needles, and is readily soluble in water and alcohol.

The salts of isobutylitamalic acid do not crystallise, and are more sparingly soluble in hot than in cold water, and almost insoluble in alcohol. The *barium* salt, $C_9H_{14}O_5Ba$, prepared by boiling the paraconic acid with baryta-water, and the *calcium* salt are anhydrous. The *silver* salt, $C_9H_{14}O_5Ag_2$, is slowly decomposed by boiling water.

When isobutylparaconic acid is distilled, octolactone, isoctylenic acid, and isobutylitaconic acid are formed, but some of the paraconic acid passes over unchanged. The lactone is isolated in the usual manner, and the isoctylenic acid is separated from the isobutylparaconic acid and isobutylitaconic acid by distillation with steam.

Isoctylenic acid, $CH_2Pr^{\beta}\cdot CH\colon CH\cdot CH_2\cdot COOH$, is a colourless oil, boils at 231—232°, and is specifically lighter than, and almost insoluble in, water. The *silver* salt, $C_8H_{13}O_2Ag$, separates from boiling water in a flocculent condition. The *barium* salt, $(C_8H_{13}O_2)_2Ba$, is more sparingly soluble in hot than in cold water, and only sparingly soluble in alcohol. The *zinc* salt and the *lead* salt are amorphous.

γ-Bromisoctylic acid, $CH_2Pr^{\beta}\cdot CHBr\cdot CH_2\cdot CH_2\cdot COOH$, prepared by treating the unsaturated acid with cold concentrated hydrobromic acid, is a heavy, yellowish oil; it is converted into isoctolactone and isoctylenic acid by dilute sodium carbonate.

Isoctolactone, $CH_2Pr^{\beta}\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ O\text{---}CO\end{matrix}>$, is a colourless liquid, volatile with steam, and only sparingly soluble in cold, but more readily in hot, water; when boiled with baryta-water, it yields the barium salt of hydroxyisoctylic acid as a yellowish, gum-like mass, soluble in hot alcohol, but only sparingly soluble in water.

Isobutylitaconic acid, $CH_2Pr^{\beta}\cdot CH\colon C(COOH)\cdot CH_2\cdot COOH$, is obtained, together with isobutylparaconic acid, when the acid solution which remains after distilling the isoctylenic acid with steam (see above) is extracted with ether. The mixture of acids is treated with water, neutralised with calcium carbonate in the cold, and the filtered solution heated to boiling, whereon *calcium isobutylitaconate*, $C_9H_{12}O_4Ca$, is deposited; the salt is washed with hot water, decomposed with hydrochloric acid, and the itaconic acid recrystallised from boiling water. It melts at 162°, being converted into the anhydride.

F. S. K.

Valeraldehyde and Pyrotartaric Acid. By R. FITTIG and F. FEIST (*Annalen*, **255**, 108—125; compare Abstr., 1888, 251, and 1886, 47). —α- and β-Methylisobutylparaconic acids are obtained as follows:—A mixture of valeraldehyde, sodium pyrotartrate, and acetic anhydride is heated at 110—120° for about 30 hours, then treated with water, the unchanged aldehyde and the acetic acid distilled with steam, the residual solution filtered and extracted with ether. The residue

obtained on evaporating the ether is dissolved in sodium carbonate, the alkaline solution shaken with ether, then acidified, and the lactonic acids extracted with ether. A small quantity of the lactonic acids remains, as sodium salts, in the original acetic acid solution, and can be isolated by extracting the strongly acidified solution with ether, evaporating the extract, and dissolving the two lactonic acids in chloroform, in order to free them from pyrotartaric acid. The two methylisobutylparaconic acids obtained in this way can only be separated with difficulty.

α-Methylisobutylparaconic acid, $CO<\begin{matrix} O \text{——} CH\cdot CH_2Pr^{\beta} \\ CHMe\cdot CH\cdot COOH \end{matrix}$, crystallises from water in plates or prisms, and from benzene in needles, melting at 142°. It is readily soluble in ether, alcohol, chloroform, and hot benzene, but almost insoluble in light petroleum and carbon bisulphide. The *barium* salt, $(C_{10}H_{15}O_4)_2Ba + 2H_2O$, prepared by neutralising a cold aqueous solution of the acid with barium carbonate, crystallises in slender needles, and is readily soluble. The *calcium* salt $(+2H_2O)$ is a colourless, semi-crystalline compound. The *silver* salt, $C_{10}H_{15}O_4Ag$, forms small, granular crystals, and is very stable.

Barium methylisobutylitamalate, $C_{10}H_{16}O_5Ba + 2H_2O$, is obtained when the paraconic acid is boiled with baryta-water; it is more readily soluble in cold than in hot water. The *calcium* salt $(+2H_2O)$ is almost insoluble in both hot and cold water. The *silver* salt, $C_{10}H_{16}O_5Ag_2$, is very unstable.

When α-methylisobutylparaconic acid is distilled, carbonic anhydride is rapidly evolved; the principal product is isobutylbutylene, but small quantities of methylisobutylbutyrolactone, α-isononylenic acid, and valeraldehyde are also obtained. The distillate is treated with sodium carbonate, the neutral products extracted with ether, and boiled with baryta-water to decompose the lactone, which is thereby converted into *barium hydroxynonylate*, $(C_9H_{17}O_3)_2Ba$. The aldehyde and hydrocarbon are then distilled with steam, and the valeraldehyde separated by shaking with a concentrated solution of sodium hydrogen sulphite; the α-isononylenic acid is isolated from the alkaline solution, after acidifying, by distilling with steam.

Isobutylbutylene (octylene), C_8H_{16}, is a colourless liquid boiling at 111·5—112·5°; it combines with bromine yielding the *dibromide*, $C_8H_{16}Br_2$, as a colourless oil.

α-Isononylenic acid, $CH_2Pr^{\beta}\cdot CH:CH\cdot CHMe\cdot COOH$, is a colourless oil boiling at 235—240° with partial decomposition. The *calcium* salt, $(C_9H_{15}O_2)_2Ca + 3H_2O$, crystallises in small needles, and is readily soluble in water. The *silver* salt, $C_9H_{15}O_2Ag$, is stable and moderately easily soluble in warm water.

β-Methylisobutylparaconic acid, $CO<\begin{matrix} O \text{—} CH_2\cdot CH_2Pr^{\beta} \\ CH_2\cdot CMe\cdot COOH \end{matrix}$ (see above), melts at 83°, and shows the same behaviour with solvents as the corresponding α-acid, only it is rather more sparingly soluble. The *barium* salt $(+4H_2O)$ is obtained by treating the acid with barium carbonate in cold aqueous solution; it crystallises in prisms, and is

very readily soluble. The *calcium* salt ($+2H_2O$) forms small, feathery crystals. The *silver* salt, $C_{10}H_{15}O_4Ag$, is soluble in hot water.

Calcium β-methylisobutylitamalate, $C_{10}H_{16}O_5Ca + H_2O$, prepared by boiling the paraconic acid with lime-water, is insoluble in water. The *barium* salt is anhydrous and almost insoluble in water. The *silver* salt, $C_{10}H_{16}O_5Ag_2$, is sparingly soluble in hot water and very stable.

When β-methylisobutylparaconic acid is distilled, it yields a hydrocarbon boiling at 111·5°, a lactone, and β-isononylenic acid. *Calcium β-isononylenate*, $(C_9H_{15}O_2)_2Ca + 3H_2O$, crystallises in needles, and is rather sparingly soluble in water. The *silver* salt, $C_9H_{15}O_2Ag$, is moderately stable and soluble in warm water. F. S. K.

Œnanthaldehyde and Pyrotartaric Acid. By R. FITTIG and R. RIECHELMANN (*Annalen*, **255**, 126—142; compare Abstr., 1888, 251).—Two isomeric methylhexylparaconic acids are formed when œnanthaldehyde is heated at 120—130° for 20 hours with sodium pyrotartrate and acetic anhydride. The product is treated with water, the unchanged aldehyde distilled with steam, and the residual solution extracted with ether. The oil obtained in this way is dissolved in sodium carbonate, the slightly alkaline solution shaken with a little calcium chloride solution and, after filtering, extracted with ether to free it from resinous products. The solution is then acidified strongly, the acids extracted with ether, repeatedly evaporated with water to expel acetic acid, and then dissolved in chloroform. On evaporating the chloroform solution, the two paraconic acids are obtained in an oily condition. The α-compound can be obtained in crystals by dissolving the mixture in carbon bisulphide and fractionally precipitating with light petroleum; in order to isolate the β-acid, the acids in the mother liquors are first purified by converting them into calcium salts, and then crystallised from a mixture of ether and light petroleum, the two kinds of crystals being separated mechanically.

α-Methylhexylparaconic acid, $CO<\begin{matrix}O\text{———}CH\cdot C_6H_{13}\\ CHMe\cdot CH\cdot COOH\end{matrix}$, crystallises from water and carbon bisulphide in colourless plates, and from a mixture of ether and light petroleum in long, slender needles melting at 101°·5. It is very readily soluble in ether, alcohol, chloroform, carbon bisulphide, and benzene, but only very sparingly in water and light petroleum; it is not volatile with steam. The *calcium* salt, $(C_{12}H_{19}O_4)_2Ca + 5H_2O$, is obtained by neutralising an aqueous solution of the acid with calcium carbonate in the cold; it crystallises in needles and is readily soluble in water and alcohol. The *barium* salt ($+3H_2O$) crystallises in needles and is readily soluble in both alcohol and water. The *silver* salt, $C_{12}H_{19}O_4Ag$, separates from water in colourless needles and is very stable. The *lead*, *copper*, *mercury*, and *ferrous* salts are insoluble in water, but readily soluble in ether.

Calcium methylhexylitamalate, $C_{12}H_{20}O_5Ca + H_2O$, prepared by boiling the lactonic acid with lime-water, is very sparingly soluble in

water and insoluble in alcohol. The *barium* salt ($+ 2H_2O$) is very sparingly soluble in cold water. The *silver* salt, $C_{12}H_{20}O_5Ag_2$, is insoluble in water and very unstable; the *copper*, *iron*, *lead*, and *mercury* salts are insoluble in ether and alcohol.

The distillation products of α-methylhexylparaconic acid are decylene, œnanthaldehyde, pyrotartaric acid (or its anhydride), and traces of other compounds, but a considerable quantity of the acid passes over unchanged.

Decylene (*hexylbutylene*), $C_{10}H_{20}$, boils at 160—161°, and yields the dibromide, $C_{10}H_{20}Br_2$, as a yellow oil when it is treated with bromine in cold carbon bisulphide solution.

β-Methylhexylparaconic acid, $CO<\begin{matrix}O\text{—}CH\cdot C_6H_{13}\\ CH_2\cdot CMe\cdot COOH\end{matrix}$, separates from carbon bisulphide in small crystals, and from a mixture of ether and light petroleum in large, cubical forms melting at 83°. It is readily soluble in ether, alcohol, chloroform, and benzene, but only moderately easily in carbon bisulphide and hot water. The *calcium* salt, with $2H_2O$, crystallises in slender needles and is readily soluble in water. The *barium* salt, with $3H_2O$, separates from water in well-defined prismatic crystals. The *silver* salt is moderately easily soluble in water and crystallises from dilute alcohol in slender needles.

Calcium methylhexylitamalate, $C_{12}H_{20}O_6Ca$, is sparingly soluble in hot water. The *barium* salt, with H_2O, separates from hot water, in which it is very sparingly soluble, in slender needles. The *silver* salt, $C_{12}H_{20}O_5Ag_2$, is insoluble in boiling water and is not very stable.

F. S. K.

Synthesis of Fumaric Acid. By E. H. KEISER (*Amer. Chem. J.*, **12**, 99—102).—According to Wislicenus' views of molecular structure, two varieties, an axially- and a plane-symmetrical, of acetylene diiodide should exist, corresponding respectively with fumaric and maleïc acids. The author has prepared these by passing acetylene through absolute alcohol containing crystals of iodine until the iodine disappeared. One variety of acetylene diiodide is an unstable liquid, decomposing when heated, and even when distilled with steam. The other is solid, and is much more stable, subliming without decomposition; it is, therefore, probably the axially symmetrical variety. When boiled successively with potassium cyanide and aqueous potash, the latter variety yields a considerable quantity of potassium fumarate. The research is still in progress.

C. F. B.

Dibromotricarballylic Acid. By E. GUINOCHET (*Compt. rend.*, **110**, 350—352).—Dibromotricarballylic acid is formed, together with the dibromide of monobromaconitic acid (Abstr., 1889, 588) by the action of bromine (4 equivalents) on aconitic acid (1 equivalent) at 115—120°, and is separated from it by means of the solubility of the dibromotricarballylic acid in water. It forms slender, prismatic needles of the composition $C_6H_6Br_2O_6+\frac{1}{2}H_2O$, very soluble in water, alcohol, and ether, and readily forming supersaturated solutions. Its salts are formed by mixing its solution with a con-

centrated solution of the particular base until neutral to phenolphthalein, and evaporating rapidly in a vacuum at the ordinary temperature. The *potassium salt*, $C_6H_3Br_2O_6K_3+3H_2O$, is a crystalline powder which decomposes at 130°; the *calcium salt*, $(C_6H_3Br_2O_6)_2Ca_3+4H_2O$, forms a vitreous solid which decomposes at 100° and is very soluble in cold water, forming a solution from which alcohol precipitates the anhydrous salt; the *barium salt*, $(C_6H_3Br_2O_6)_2Ba_3+5H_2O$, is a white, amorphous solid which does not alter at 100°, but decomposes at 115°.

Dibromotricarballylic acid melts below 100° and evolves hydrogen bromide, and on further heating, decomposes. If the fused but not discoloured substance is redissolved in water, it yields a crystalline mass with the properties of the original product. In a vacuum the acid loses weight continually, and the percentage of bromine and the basicity gradually increase. It does not decompose in solution in the cold. In presence of nitric acid, silver nitrate precipitates half the bromine. The aqueous solution decomposes when heated, and if silver nitrate is added, silver bromide is precipitated in quantity varying with the conditions of the experiment.

With sodium amalgam, dibromotricarballylic acid yields ordinary tricarballylic acid. C. H. B.

Guinochet's Isomeric Tricarballylic Acid. By R. Demuth and V. Meyer (*Ber.*, **23**, 529—531).—The tribromotricarballylic acid obtained by Guinochet (Abstr., 1889, 588) by heating aconitic acid with bromine is, in reality, dibromosuccinic acid, and Guinochet's isomeric tricarballylic acid (this vol., p. 238) is succinic acid.

F. S. K.

Action of Sodium and Potassium Ethoxides on Ethyl Tartrate. By E. Mulder (*Rec. Trav. Chim.*, **8**, 361—385).—Sodium was dissolved in pure anhydrous alcohol, and a slight excess of ethyl tartrate added. The mixture was placed in a flask connected with a vessel containing sulphuric acid, and a vacuum was established; at intervals the flask was weighed. The weight finally obtained corresponded with the formation of *ethyl sodiotartrate*, COOEt·CH(ONa)·CH(OH)·COOEt, but it seemed that some compounds of this with one or more molecules of alcohol were first formed. It forms a vitreous mass very soluble in pure alcohol, and insoluble in ether or benzene. It is very deliquescent, but is decomposed by water, alcohol, and ethyl sodium tartrate,

COONa·CH(OH)·CH(OH)·COOEt,

being formed; the latter is at once formed when ethyl tartrate is treated with sodium and ordinary absolute alcohol, which always contains some water.

Ethyl disodiotartrate, $C_2H_2(ONa)_2(COOEt)_2$, was prepared in the same way as the monosodium compound, half the weight of ethyl tartrate being used; it was found advantageous to work in an atmosphere of hydrogen. In its properties this substance resembles the

monosodium compound; when it is decomposed by water, normal sodium tartrate is formed. *Mono-* and *di-potassium* compounds have also been prepared, and are still undergoing investigation.

The author has used ethyl chloride or iodide as a means of ascertaining whether a reaction has taken place. Sodium ethoxide dissolved in pure alcohol was added to a slight excess of ethyl tartrate, and then ethyl chloride was added, and the whole sealed up in a tube. If a reaction has taken place, since the ethyl tartrate was in excess, all the ethoxide will have been used up, and nothing will be observed when the ethyl chloride is added. But if no reaction has taken place, the ethyl chloride and sodium ethoxide will react, forming ether and sodium chloride, and the latter, being insoluble in alcohol, will be precipitated. In no case was a precipitate formed, and it was thus shown that the reactions had taken place as described above. In all cases another tube was taken, for the sake of comparison, containing the same quantities of the same substances (except the ethyl tartrate) as the first; this was submitted to the same conditions, and always gave a precipitate of sodium chloride, &c. C. F. B.

Preparation of Levulosecarboxylic Acid. By H. KILIANI and G. DÜLL (*Ber.*, **23**, 449—452).—In order to prepare levulosecarboxylic acid in large quantities for an examination of its behaviour on oxidation, the authors have endeavoured to improve the method previously adopted. An attempt was made to isolate the acid in the form of its phenylhydrazide, according to Fischer and Passmore's method (this vol., p. 152), but even when pure levulosecarboxylic acid was used as the starting point, the phenylhydrazide does not crystallise out until the solution has been evaporated to a syrup and allowed to remain for some time. After recrystallisation from alcohol, it melts at 162°, decomposes at 188°, and gives the characteristic coloration with ferric chloride in aqueous, but not in sulphuric acid solution. No phenylhydrazide could be isolated from the dark-red syrup into which levulosecyanhydrin passes after a time, although this must contain at least 50 per cent. of the ammonium salt of the acid; it was, therefore, necessary to return to the old method, in which, however, certain improvements have been made.

The levulose is obtained according to Hönig's directions (Abstr., 1888, 247) in such a manner as to contain 25—30 per cent. of water; to this an equivalent quantity of 50 per cent. hydrocyanic acid is added, together with a drop of dilute ammonia, and if possible a fragment of ready-formed cyanhydrin. The bottle is tightly stoppered, and allowed to remain in cold water until the whole has completely solidified ($\frac{1}{2}$—1 hour), then stirred with 92 per cent. alcohol, collected, washed with alcohol, and dried in a vacuum over sulphuric acid. The pure and dry cyanhydrin thus obtained may be preserved for months, whereas the impure compound decomposes almost immediately. For its hydrolysis, 10 grams are treated with 20 grams of hydrochloric acid, saturated at the ordinary temperature, and allowed to remain two hours after the separation of ammonium chloride has ceased, then diluted with an equal volume of water, and evaporated

on the water-bath to a thin syrup. This is extracted with water, and the solution again evaporated three times, the final syrup dissolved in water, filtered, treated with barium hydroxide, and evaporated. The solution is then saturated with carbonic anhydride, decolorised by animal charcoal, the barium precipitated by dilute sulphuric acid, and the remaining trace of hydrochloric acid by silver oxide. The filtrate on evaporation yields a syrup, which, on stirring and adding a crystal of the ready formed lactone, crystallises completely within a few hours. The levulosecarboxylic lactone thus obtained is sufficiently pure for most purposes, but may be further purified by crystallisation from alcohol. This lactone and also that of dextrosecarboxylic acid yield beautifully crystalline compounds with ammonia, and the former compound gives a polybasic acid on oxidation with nitric acid. H. G. C.

Reduction of the Acids of the Sugar-group. By E. FISCHER (*Ber.*, **23**, 930—938).—The method of reducing acids of the sugar-group by means of sodium amalgam (Fischer, Abstr., 1889, 1149; this vol., p. 466) has been extended to a large number of monobasic and to some bibasic acids, with results which are now communicated in a preliminary form. As already pointed out (this vol., p. 471), this reaction is applicable only to those acids which form lactones, since it is the lactone which undergoes reduction; acids like mucic and gluconic acids, which either do not form lactones or only undergo conversion into lactones partially and under special conditions, and salts of the acids, whether lactone-forming or not, are not affected by treatment with sodium amalgam. It is on this account, therefore, that the reduction is carried on in solutions which are kept acid by the frequent addition of small quantities of sulphuric acid. In order to obtain the largest yield of sugar (40—60 per cent.), it is necessary to use the pure, crystallised lactone; when this cannot be obtained, as in the case of gluconic or saccharic acids, the aqueous solution of the acid is concentrated to a syrup and heated on a water-bath or at higher temperatures for many hours, with the object of forming as much lactone as possible. Details of the method adopted for the reduction of the monobasic acids and of the method of purifying the product are given in the paper, but do not differ in any important points from those already communicated (compare this vol., p. 466). Unlike the monobasic acids of the sugar-group, the bibasic acids do not yield sugars, but aldehyde-acids, and consequently a different process is necessary for the isolation and purification of the product; this is described in connection with the reduction of saccharic acid (*vide infra*).

Regarding lactones as "internal" ethereal salts, the author has instituted experiments with the object of ascertaining to what extent it is possible to reduce the ethereal salts of acids of the sugar-group and of other monobasic and bibasic acids which do not form lactones, and finds that ethyl mucate is reduced to an aldehyde-acid by sodium amalgam. The amides of the acids, however, do not undergo reduction by sodium amalgam in acid solution, thus differing from the amides of aromatic acids (compare Guareschi, this Journal, 1875, 569).

Kiliani's method of forming carboxy-acids by treating carbohydrates of the sugar-group with hydrogen cyanide (Abstr., 1886, 219, 438, 526, 869; 1887, 229, 465), combined with the author's method of reducing these acids to the corresponding carbohydrates by means of sodium amalgam, has made it possible to effect the synthesis of sugars containing 7 and 8 atoms of carbon in the molecule (*vide infra*), and the limit to which this process can be carried has not yet been reached. It becomes necessary, therefore, to adopt some system of nomenclature for carbohydrates of this group. The author proposes to employ the terms pentose, heptose, octose, &c., for the sugars, pentitol, heptitol, octitol, &c., for the corresponding alcohols, and heptonic acid, octonic acid, &c., for the acids of the series, according to the number of carbon-atoms in the compounds. A prefix, having reference to the source of the compound, is employed to distinguish the individual substances; thus, the compounds obtained from mannose receive the names mannoheptose, mannoctose, mannoheptitol, mannoctonic acid, &c., those from galactose, galaheptose, &c., those from dextrose, glucoheptose, &c. In view of the fact that an optically inactive and a dextrorotatory modification of levulose have been obtained, and the probability that corresponding compounds of dextrose will soon be prepared (this vol., p. 469), the author proposes to discard these names as misleading, and substitute glucose and fructose for dextrose and levulose respectively. The difficulty which arises from the use of the word glucose as a generic term for the 6-carbon sugars, as well as a synonym for dextrose, can easily be met by adopting the term hexose for this class of sugars.

The following preliminary notes of investigations carried on in conjunction with the author's pupils are communicated:—

Monobasic Acids.—(1.) The reduction of d.-, i.-, and l.-mannonic acids to the corresponding mannoses, and of gluconic acid to d.-glucose (ordinary dextrose) (this vol., p. 466), has already been described.

(2.) Galactonic acid.—The lactone of galactonic acid is present in considerable quantities in the syrup obtained by evaporating an aqueous solution of the acid on a water-bath, and on reduction yields ordinary galactose.

(3.) Mannosecarboxylic acid.—The lactone of this acid, on reduction, yields about 50 per cent. of *mannoheptose*, a dextrorotatory crystalline compound. The *phenylhydrazone* is sparingly soluble in cold water, and melts at 188—190° with decomposition; the *osazone* forms yellow needles, melts at 198—200° with decomposition, and is insoluble in water. On further reduction, mannoheptose is converted into *mannoheptitol*, $C_7H_{16}O_7$, which is identical with perseïtol (Maquenne, Abstr., 1889, 32). On oxidation with dilute nitric acid, mannoheptitol (perseïtol) is reconverted into mannoheptose.

Mannoheptose reacts with hydrogen cyanide, and the resulting *mannoctonic acid* forms a beautifully crystalline *lactone* which melts at 167—170°, and has a specific rotation of $[\alpha]_D = -43.58$. On reduction, the lactone yields dextrorotatory *mannoctose*, which is charac-

terised by forming a sparingly soluble *phenylhydrazone*, $C_8H_{16}O_7 \cdot N_2HPh$, melting at 212—213°.

(4.) Glucosecarboxylic acid.—*Glucoheptose*, obtained from the lactone of this acid by reduction, crystallises from water in beautiful tables which melt at about 190° with decomposition. The *phenylhydrazone* is readily soluble in water; the *osazone* forms golden-yellow needles and melts at 197° with decomposition. On treatment with hydrogen cyanide, glucoheptose yields *glucoctonic acid*, from which a well-crystallised *barium* salt, $(C_8H_{15}O_9)_2Ba$, has been prepared.

(5.) Galactosecarboxylic acid.—The *lactone* of galactosecarboxylic acid is obtained by the prolonged heating of a syrupy aqueous solution of the acid on a water-bath, and forms colourless crystals melting at 149—150°. On reduction it is converted into *galaheptose*, which forms a sparingly soluble *phenylhydrazone* melting at about 199° with decomposition, and an *osazone* melting at about 220° with decomposition. Galaheptose interacts with hydrogen cyanide.

(6.) Rhamnosecarboxylic acid.—A 50 per cent. yield of a *methylhexose*, $OH \cdot CMeH \cdot [CH \cdot OH]_4 \cdot CHO$, is obtained by the reduction of the lactone of this acid. This carbohydrate crystallises well from methyl alcohol and melts at 180—181°. The *phenylhydrazone* is readily soluble; the *osazone* melts at about 200° with decomposition. On treatment with hydrogen cyanide, it yields a *methylheptonic acid*. The *lactone* of this acid, $C_8H_{14}O_7$, crystallises well, and on reduction is converted into a *methylheptose*, which forms a sparingly soluble *phenylhydrazone*.

(7.) Fructosecarboxylic (levulosecarboxylic) acid and saccharin, on reduction, afford good yields of two carbohydrates containing "branched" carbon-chains.

(8.) Carboxylic acid of Milk-sugar.—Milk-sugar reacts with hydrogen cyanide, forming a *carboxylic acid* which yields an insoluble basic *lead* salt, does not reduce Fehling's solution, and is readily hydrolysed by boiling with dilute sulphuric acid. When evaporated to a syrup and reduced, the acid is converted into a sugar which probably has the formula $C_{13}H_{24}O_{12}$.

Bibasic Acids.—(1.) Saccharic acid.—The lactone of saccharic acid, obtained by heating the aqueous solution of the acid on a water-bath, is converted, on reduction, into an acid which reduces Fehling's solution, and shows a great resemblance to glycuronic acid. This aldehyde-acid is purified by adding neutral lead acetate to the reduction-product rendered slightly acid by acetic acid, whereby sulphuric acid and the regenerated saccharic acid are precipitated; the filtrate is then precipitated by the addition of basic lead acetate, the precipitate decomposed by dilute sulphuric acid, any excess of sulphuric acid being removed by means of baryta, and the filtrate evaporated to a syrup in a vacuum. The aldehyde-acid has not yet been crystallised.

(2.) Mucic acid.—When a $2\frac{1}{2}$ per cent. aqueous solution of ethyl mucate is reduced by sodium amalgam in the usual way, an aldehyde-acid is formed. This can be purified by the method just described, and is a pale-yellow syrup which reduces Fehling's solution, and on oxidation is reconverted into mucic acid. W. P. W.

Constituents of Iceland Moss. By A. HILGER and O. BUCHNER (*Ber.*, **23**, 461—464).—The authors have reinvestigated the preparation and properties of lichenstearic and cetraric acids, which were first examined by Knop and Schnedermann (*Annalen*, **55**, 164), Herberger (*Annalen*, **21**, 137), and Bolley (*Annalen*, **54**, 143; **86**, 50), and have obtained the following results:—

Lichenstearic acid is best prepared by extracting the powdered flakes of Iceland moss with light petroleum, evaporating the solution, and boiling the residue with water, sodium carbonate being added in such quantity that a portion of the substance remains undissolved. To the filtered solution, an excess of hydrochloric acid is added, the precipitate well pressed and repeatedly crystallised from light petroleum, and the solution decolorised by animal charcoal. It is then further recrystallised several times from boiling alcohol, and is thus obtained as a voluminous, white mass consisting frequently of stellate groups of small prisms, which speedily fall into small, lustrous plates. It melts at 120°, and is soluble in alcohol, chloroform, benzene, and light petroleum, but is almost insoluble in water. Its alkaline salts are the only ones soluble in water, and it is not acted on by acetic chloride. It yields a chloride with phosphoric chloride, and from the analysis of this compound, the free acid, and certain salts, it appears to be a bibasic acid of the formula $C_{13}H_{76}O_{13}$. It is converted on oxidation into carbonic anhydride and capric acid.

Cetraric acid is best obtained by Knop and Schnedermann's process, with the alteration that the precipitate formed by hydrochloric acid is extracted with light petroleum to remove lichenstearic acid, and the colouring matter removed by a mixture of ether and turpentine oil. It decomposes at about 200°, and appears also to be a bibasic acid, the most probable formula being $C_{30}H_{30}O_{12}$. H. G. C.

Chloropyromucic Acids. By H. B. HILL and L. L. JACKSON (*Amer. Chem. J.*, **12**, 112—130; compare this vol., p. 482).—*Dichloropyromucic acid* [COOH : Cl_2 = 2 : 4 : 5 or 2 : 3 : 5] was prepared, together with an isomeric acid [2 : 3 : 5], by distilling ethyl pyromucate tetrachloride at 16 mm. pressure. It melts at 197—198°, and sublimes unchanged below its melting point. It dissolves in ether, alcohol, and hot water; 100 parts of water at 19·5° dissolve 0·13 part of the acid. The *barium* and *calcium salts* (both with 4 mols. H_2O) were prepared. Of these, 100 parts of water at 19·5° dissolve 1·58 and 6·85 parts respectively. *Ethyl dichloropyromucate* [2 : 4 : 5 or 2 : 3 : 5] melts at 72—73°, and boils at 122·5° under a pressure of 16 mm. This dichloropyromucic acid is reduced by sodium amalgam to pyromucic acid. With bromine and water, it reacts like the [2 : 3 : 5] acid previously described, giving chlorofumaric acid. When heated over a water-bath with concentrated hydrochloric acid, a substance of the formula $C_4H_3ClO_2$ is formed, according to the equation $C_5H_2Cl_2O_3 + H_2O = C_4H_3ClO_2 + CO_2 + HCl$. This substance is soluble in chloroform and benzene, and slightly in water and light petroleum; when crystallised from this last solvent, it forms slender prisms which melt at 52—53° and sublime rapidly at ordinary temperatures. It reduces silver oxide, and gives a yellow solution with aqueous alkalis. By

the action of fuming sulphuric acid on dichloropyromucic acid [2 : 4 : 5 or 2 : 3 : 5], a *dichlorosulphopyromucic acid* is formed, the *barium hydrogen* and *barium* (with 2 mols. H_2O) *salts* of which were prepared. Sufficient data are not available to determine whether this dichloropyromucic acid has the formula [COOH : Cl_2 = 2 : 4 : 5] or [2 : 3 : 5]; the authors incline to the latter view, and look on it as the geometrical isomeride of the [2 : 3 : 5] acid described in a previous paper.

Trichloropyromucic acid [COOH : Cl_3 = 2 : 3 : 4 : 5] was prepared by decomposing the tetrachloride of the [2 : 5] chloropyromucic acid. Ethyl pyromucate was chlorinated at 145° until one hydrogen-atom had been replaced by chlorine; the temperature was then allowed to fall to 120°, and the chlorination continued to saturation. The product (tetrachloride of ethyl chloropyromucate) was treated with alcoholic soda, the sodium salt formed was decomposed with hydrochloric acid, and the acid thus obtained was purified by recrystallising its ammonium salt from water; the yield of acid was only 15 per cent. of the theoretical. Trichloropyromucic acid melts at 172—173°, and dissolves in alcohol, ether, and boiling benzene, and slightly in hot water; 100 parts of water at 19·5° dissolve 0·13 part of it. The *barium* and *calcium salts* (each with 4 mols. H_2O) were prepared; 100 parts of water at 19·5 dissolve 0·27 and 0·64 part of these respectively. The *potassium* and *silver salts* were found to be anhydrous. *Ethyl trichloropyromucate* was prepared by warming an alcoholic solution of the acid with concentrated sulphuric acid; it crystallises in flat prisms melting at 62—63°. *Trichloropyromucamide* was prepared by the action of solid ammonium carbonate on the acid chloride; it crystallises in long, slender needles melting at 160—161°. Trichloropyromucic acid, when treated with bromine and water, gives both *trichlorobromofurfuran* and dichloromaleïc acid. When oxidised with nitric acid, it yields dichloromaleïc acid.

Dichlorobromopyromucic acid [COOH : Cl_2 : Br = 2 : 3 : 4 : 5] is formed when dichloropyromucic acid [2 : 3 : 4] is exposed to the vapour of bromine at the ordinary temperature. It melts at 185—186°, and dissolves in alcohol, ether, and boiling benzene.

Dibromochloropyromucic acid [COOH : Br_2 : Cl = 2 : 3 : 4 : 5] was prepared by treating ethyl dibromopyromucate [2 : 3 : 4] with chlorine and decomposing the product with alcoholic soda. It melts at 193—194°, and dissolves in alcohol, ether, and boiling benzene.

Dichloronitropyromucic acid [COOH : Cl_2 : NO_2 = 2 : 3 : 4 : 5] was obtained by dissolving dichloropyromucic acid [2 : 3 : 4] in fuming sulphuric acid, isolating the sulphonic acid thus formed, and treating it with a mixture of fuming nitric acid and concentrated sulphuric acid. It melts at 189—190°, and dissolves in alcohol and ether, and in hot benzene or water.
C. F. B.

Constitution of Methylpyromucic Acid. By H. B. Hill and W. S. Hendrixson (*Ber.*, **23**, 452—453).—The methylfurfuraldehyde described by Hill in a former paper has since been obtained by Maquenne (this vol., p. 33), and Bieler and Tollens (this vol., p. 238),

from fucusol, and also by the action of sulphuric acid on rhamnose (isodulcitol); from the last-named formation it would appear to be δ-methylfurfuraldehyde. This supposition has been confirmed by the authors' examination of the methylpyromucic acid obtained by its oxidation, which is resolved by the action of bromine-water into a ketonic acid of the formula $C_5H_6O_3$. Pyromucic acid under similar conditions yields fumaraldehyde. The above ketonic acid appears to be identical with the acetoacrylic acid described by Wolff (Abstr., 1887, 465), which would naturally be formed if the methyl-group occupied the δ-position. The melting point of the acid formed was 122—123°, whereas Wolff gives 125—125·5°, and the hydrazone melts at 157°, agreeing in this and its other properties with the hydrazone of acetoacrylic acid described by Bender (Abstr., 1888, 1188), and Decker (Abstr., 1889, 49). H. G. C.

Stereochemical Studies. By J. LOSCHMIDT (*Monatsh.*, **11**, 28—32).—The author shows how by a combination of six tetrahedral carbon-atoms a formula may be obtained for benzene in which the alternate double and single linkage of the Kekulé formula is maintained, and of which the latter formula appears to be only an abbreviation. H. C.

Nitrothymol-derivatives. By G. MAZZARA (*Gazzetta*, **19**, 61—71).—*Paranitro-orthobromothymol*, $C_6HPrMeBr(NO_2)\cdot OH$ [4 : 1 : 2 : 6 : 3], is prepared by the action of nitric acid (sp. gr. = 1·46) on a solution of bromothymol in glacial acetic acid. It forms yellow crystals, melts at 107—108°, and is very sparingly soluble in water. It is identical with the compound previously described (Abstr., 1886, 1019), melting at 100—101°.

The *potassium*-derivative crystallises in small, yellow needles containing ½ mol. H_2O; on exposure to air they fall into a red powder. The *ethyl ether* forms yellow laminæ which melt at 67—69°.

Paramido-orthobromothymol is prepared by the reduction of the nitrobromothymol; it crystallises from light petroleum in pale-yellow scales, melts at 94—95°, dissolves in hot dilute alcohol and in hot benzene, and is sparingly volatile in steam. It is probably identical with the amidobromothymol previously described (*loc. cit.*), melting at 90°. The *hydrochloride* crystallises from hot alcohol in white needles, and melts at 185° with previous blackening.

Paradiacetamido-orthobromacetylthymol, $C_6HPrMeBr(NAc_2)\cdot OAc$ [4 : 1 : 2 : 6 : 3], is prepared by boiling amidobromothymol with an excess of acetic anhydride for four and a half hours. It forms pinkish-white crystals which have an odour of butyric acid, melts at 136—137°, and is soluble in alcohol and benzene. *Parabenzamido-orthobromothymol*, $C_6HPrMeBr(NHBz)\cdot OH$ [4 : 1 : 2 : 6 : 3], is prepared by heating a mixture of amidobromothymol and benzoic chloride in molecular proportion, at 100—110° for five to six hours. It forms small, reddish nodules which soften at 160°, and melt at 162—164°. It is soluble in alcohol and in benzene. With potash, it forms a greenish-yellow solution, from which it is reprecipitated unchanged by hydrochloric acid.

Dinitrothymol, $C_6HPrMe(NO_2)_2\cdot OH$ [4 : 1 : 2 : 6 : 3], is obtained as

a bye-product in the preparation of nitrobromothymol; it may be prepared by the action of nitric acid (sp. gr. 1·46) on nitrobromothymol. It crystallises from light petroleum in needle-shaped prisms; melts at 55°. The *ethyl ether* melts at 52—53°, and is identical with that obtained by Ladenburg and Engelbrecht (Abstr., 1878, 60).

The chlorodinitrocymene melting at 100—101°, prepared by these authors from dinitrothymol, thus contains the two NO_2-groups in the positions 2 : 6, and the dinitro-derivative melting at 80°, obtained by Fileti and Crosa (Abstr., 1889, 494), must consequently have the constitution [$(NO_2)_2$ = 5 : 6]. S. B. A. A.

Aromatic Mercaptans. By R. Leuckart (*J. pr. Chem.* [2], **41**, 179—224).—The author's new method for obtaining aromatic mercaptans consists in acting on the diazo-aromatic compounds with potassium ethylxanthate, and decomposing the compound thus obtained with caustic alkali.

Phenyl ethylxanthate, PhS·CS.OEt, is formed (85 per cent. of theory) when diazobenzene chloride is mixed with potassium ethylxanthate (eq. mols.), and the resulting solid carefully heated; nitrogen is evolved, and the carbonate left as an oil which is purified by dissolving it in ether, washing with alkali and acid, and distilling with steam. When heated with alcoholic potash, it is converted into the potassium compound of thiophenol, from which thiophenol is obtained by the action of an acid; the yield is 70 per cent. of theory. When heated with alcoholic ammonia, it is converted into thiophenol, ethyl alcohol, and ammonium thiocyanate.

Ortho-, meta-, and *para-tolyl ethylxanthates* are obtained in like manner, and are also yellowish-red, uncrystallisable oils; with alcoholic potash, they yield ortho-, meta-, and para-thiocresols respectively. Paratolyl bisulphide (Abstr., 1879, 230) melts at 46°, not 43°.

Paratolyl symmetrical dithiocarbonate, $CO(SC_6H_4Me)_2$, is obtained as a bye-product in making paratolyl ethylxanthate in beautiful, colourless needles melting at 90—91°; when heated with alcoholic potash and then acidified with hydrochloric acid, carbonic anhydride and thioparacresol are formed, but no paracresol; this shows that it is the normal salt of the symmetrical dithiocarbonic acid, $CO(SH)_2$, and not of the isomeric acid, OH·CH·SH, a conclusion confirmed by the fact that it can be prepared by the action of carbon oxychloride on thioparacresol.

Metaxylyl ethylxanthate, similarly obtained, is a yellowish-red oil, which yields meta- (?) thioxylol (m. p. 213—214°), with alcoholic potash.

When diazo-orthohydroxybenzene chloride acts on potassium ethylxanthate, hydroxyphenyl mercaptan (b. p. 217°) [OH : SH = 1 : 2] (Abstr., 1883, 989) is obtained. When diazoparahydroxybenzene chloride is used, *monothioquinol ethylxanthate* is formed as a dark, uncrystallisable, sticky substance. *Monothioquinol* is obtained from this compound by heating it with alcoholic potash; the alcohol is distilled off, the residue dissolved in water, filtered, and saturated with carbonic anhydride; the separated oil is extracted with ether, the ether evaporated, and the oil warmed with zinc and sulphuric acid for

4—5 hours; after again separating it with ether, it is distilled under diminished pressure (45 mm.), when it boils without decomposition at 166—168°; it is a colourless liquid, solidifying to a lustrous, white, crystalline mass, which melts at 29—30°. The *lead compound* was obtained.

Monothio-ethylquinol, $OEt\cdot C_6H_4\cdot SH$, is obtained by heating monothioquinol (1·26 grams) with ethyl iodide (1·56 grams) and potassium hydroxide (0·56 gram) in alcohol for three hours; the alcohol is distilled off, the residue dissolved in ether, washed, and distilled; the quinol passes over at 275—277° as a colourless liquid, which solidifies and melts at 40—41°. It gives a yellow precipitate with lead acetate.

Ethylmonothioquinol, $OH\cdot C_6H_4\cdot SEt$, is formed when lead monothioquinol is heated for several hours with ethyl iodide in alcohol. It is a colourless, crystalline solid melting at 40—41°, and boiling at 282—287°; it is not precipitated by lead acetate.

Monothio-acetylquinol, $OAc\cdot C_6H_4\cdot SH$, obtained by treating paracetoxyphenyl bisulphide (see below) with zinc-dust and sulphuric acid at 45°, is a colourless, strongly refractive liquid of faint odour, which boils at 275—280°; its *lead compound* was obtained.

Diacetylmonothioquinol, $OAc\cdot C_6H_4\cdot SAc$, obtained by heating monothioquinol with acetic chloride at 120—130°, forms small, pearly leaflets of faint odour, and melts at 65·5—66°.

Parahydroxyphenyl bisulphide, $S_2(C_6H_4\cdot OH)_2$, is obtained by the action of the air on an ammoniacal alcoholic solution of monothioquinol; it crystallises in slender, pale-yellow needles melting at 150—151°. When heated with acetic chloride, it yields *paracetoxyphenyl bisulphide*, $S_2(C_6H_4\cdot OAc)_2$, which crystallises in pearly leaflets of faint odour, melting at 88—89°.

Metanitrothiophenol, $NO_2\cdot C_6H_4\cdot SH$, is obtained as follows:—Solutions of metanitrodiazobenzene chloride and potassium ethylxanthate are gradually mixed at 70—75°; a yellow diazo-compound separates, but quickly decomposes, evolving nitrogen, and forming a heavy, brown oil; this is dissolved in ether, the solution washed and evaporated, and the oil heated with alcoholic potash. The *potassium compound* of metanitrothiophenol thus obtained is dissolved in water, acetic acid added, and then lead acetate, which gives a dark-yellow precipitate; this is washed with water, suspended in alcohol, and decomposed by hydrogen sulphide. The phenol is a dark-yellow oil, easily oxidised by the air or other agents to *metanitrophenyl bisulphide*, $S_2(C_6H_4\cdot NO_2)_2$, which forms yellowish, well-formed, rhombic crystals, or soft, aggregated needles, melting at 84°; by reduction it yields metamidothiophenol, the *lead compound* of which is described.

Paranitrophenyl bisulphide.—Paranitraniline (2 grams) is diazotised and mixed with a warm solution of potassium ethylxanthate (2·3 grams); a yellowish-red oil separates and is dissolved in ether, washed, and saponified; the bisulphide thus obtained forms beautifnl, small crystals melting at 168—170°. With zinc-dust and acetic acid, it yields paranitrothiophenol; but with zinc and sulphuric acid, it yields paramidophenyl bisulphide (see below).

Paramidophenyl ethylxanthate, $EtO\cdot CS\cdot S\cdot C_6H_4\cdot NH_2$, is obtained as

an amorphous, brown, soft, wax-like mass when the product of the action of paranitrodiazobenzene chloride on potassium ethylxanthate is dissolved in ammonia and treated with hydrogen sulphide; it is also obtained by the action of hydrogen sulphide on the alcoholic ammoniacal solution of azobenzene ethylxanthate (see below). When it is saponified with alcoholic potash, *paramidothiophenol* is obtained.

Acetylparamidophenyl ethylxanthate, $EtO\cdot CS\cdot SC_6H_4NHAc$, is prepared by diazotising acetylparaphenylenediamine, and mixing the diazotised solution with potassium ethylxanthate at 60—70°, washing the precipitate thus formed with strong hydrochloric acid, drying, and recrystallising: it crystallises in thin, pale-yellow leaflets melting at 151°; it is insoluble in water and light petroleum, but soluble in alcohol, ether, glacial acetic acid, and benzene. When it is heated for 20—30 hours with alcoholic potash, the alcohol distilled off, and acetic acid added, paracetamidophenyl bisulphide (Abstr., 1878, 974) is formed; when this is reduced with zinc-dust in acetic acid and precipitated with lead acetate, a lead compound is obtained which, on being decomposed with hydrogen sulphide, yields *acetylparamidothiophenol*, $SH\cdot C_6H_4\cdot NHAc$; this crystallises in beautiful leaflets melting at 163°, and soluble in most solvents.

Paramidophenyl bisulphide is identical with Schmidt's pseudodithioaniline (Abstr., 1878, 974); if it is diazotised and the solution mixed with soda, a yellow flocculent precipitate is formed, which melts at 150—151°; if the diazotised solution is mixed with potassium ethyl xanthate, and the product saponified, dithioquinol (m. p. 98°, Abstr., 1877, 81) is produced.

Paraphenylene bisulphide, $C_6H_4S_2$, is produced by the oxidation of dithioquinol; it blackens without melting at 300°.

Dimethylparamidophenyl ethylxanthate, $EtO\cdot CS\cdot S\cdot C_6H_4\cdot NMe_2$, obtained by diazotising dimethylparaphenylenediamine and mixing the solution with potassium ethylxanthate, is a yellow oil which solidifies and forms yellow crystals melting at 54·5°, and soluble in the usual solvents except water. When it is heated with alkalis, or, better, with alcoholic solution of aniline at 200°, it is converted into tetramethylamidophenyl bisulphide, identical with Merz and Weith's dithiodimethylaniline (Abstr., 1886, 792); this, if treated with tin and hydrochloric acid, yields dimethylamidothiophenol (*loc. cit.*).

Azobenzene ethylxanthate, $EtO\cdot CS\cdot S\cdot C_6H_4\cdot N_2Ph$, is made by diazotising amidoazobenzene sulphate and mixing the solution with potassium ethylxanthate; it forms brilliant, vermilion-red aggregates of crystals melting at 65°.

Azobenzene bisulphide, $S_2(C_6H_4\cdot N_2Ph)$, formed when the last-mentioned compound is saponified with alcoholic potash, crystallises in yellow leaflets melting at 162°.

By saponifying the product of the action of tetrazodiphenyl sulphate (from the diazotising of benzidene sulphate) on potassium ethylxanthate, diphenyl dihydrosulphide (m. p. 176°, Gabriel and Deutsch, Abstr., 1880, 477) is obtained; when methyl chloride is passed into an alcoholic solution of this, containing caustic potash, *diphenyl dithiodimethyl ether*, $C_{12}H_8(SMe)_2$, is precipitated; it crystallises in

soft, pale-yellow leaflets melting at 184°. The corresponding *ethyl compound*, $(C_6H_4{\cdot}SEt)_2$, obtained in like manner, crystallises in beautiful, silvery leaflets melting at 135°.

Orthoditolyl dihydrosulphide, $C_{12}H_6Me_2(SH)_2$, obtained by a method similar to that for diphenyl dihydrosulphide forms beautiful, yellowish leaflets, melts at 113°, and is soluble in alcohol, ether, benzene, and aqueous potash. By oxidation, it yields a substance which crystallises in needles melting at 118°.

By the action of α-diazonaphthalene chloride on potassium ethylxanthate, α-naphthyl mercaptan is obtained, and α-naphthyl bisulphide, α-naphthyl sulphide, and α-naphthyl sulphone can be prepared from the mercaptan; these substances are already known.

Potassium sulpho-α-naphthyl ethylxanthate, $EtO{\cdot}CS{\cdot}SC_{10}H_6^{\alpha}{\cdot}SO_3K$, is obtained by the action of α-diazonaphthalenesulphonic acid (from naphthionic acid and sodium nitrite) on potassium ethylxanthate; it crystallises in small, brownish leaflets. When it is heated with dilute alcoholic potash, the alcohol evaporated, and acetic acid added, a yellow precipitate of *potassium sulphonaphthyl bisulphide* $S_2(C_{10}H_6SO_3K)_2$, is obtained.

By this general method, β-naphthyl bisulphide and β-naphthyl mercaptan were also obtained; they are already known.

Potassium sulpho-β-naphthyl ethylxanthate was also obtained; when it is heated with strong alcoholic potash, the alcohol evaporated, and acetic acid added, a colourless, crystalline mass (which gives *zinc β-thionaphtholsulphonate* with zinc and sulphuric acid), and *potassium sulpho-β-naphthyl bisulphide* are obtained; the free acid and the *lead salt* of the latter were also prepared. A. G. B.

Paraxylidine. By L. Pflug (*Annalen*, **255**, 168—176).—*Formylparaxylidine*, $C_9H_{11}NO$, prepared by boiling xylidine with concentrated formic acid, crystallises from water in long, colourless needles, melts at 111—112°, and turns reddish on keeping. The *benzoyl-derivative*, $C_{15}H_{15}NO$, crystallises from alcohol in colourless needles melting at 140°. The *benzylidine*-derivative, $C_{15}H_{15}N$, crystallises from alcohol in yellowish plates, melts at 101—102°, and is decomposed by boiling acids. The *benzyl*-derivative, $C_{15}H_{17}N$, prepared by reducing the benzylidene-derivative with sodium amalgam in alcoholic solution, is a light-yellow oil, boiling at 320—325°; the *hydrochloride* crystallises in colourless needles, and is readily soluble in water. The *nitrosamine* is a yellow oil, and gives Liebermann's reaction.

Metanitrobenzylidenexylidine, prepared by warming paraxylidine with metanitrobenzaldehyde, crystallises from alcohol in yellow needles, and melts at 126°; it is only sparingly soluble in cold alcohol, ether, and light petroleum, and insoluble in water.

Dianilidoparaxyloquinone, $C_{20}H_{18}N_2O_2$, can be easily obtained from paraxyloquinone; it crystallises from hot alcohol in yellowish-brown needles, melts at 264°, and is more readily soluble than dianilidoquinone.

Methylparaxylidine is prepared by boiling formylxylidine with potash and methyl iodide in methyl alcoholic solution, and heating the product with concentrated hydrochloric acid. It is a yellowish

oil, boils at 225—227° (735 mm.), and is readily volatile with steam.

Paramethylxylylnitrosamine, $C_9H_{12}N_2O$, is prepared by treating methylxylidine with sodium nitrite and dilute sulphuric acid in ice-cold aqueous solution; it is a yellow oil.

Paranitrosoparamethylxylidine, $C_9H_{12}N_2O$, is obtained by dissolving the preceding compound in ether, gradually adding alcoholic hydrochloric acid to the well-cooled solution, and decomposing the salt thus produced with ammonia. It crystallises from benzene or alcohol in green needles with a blue reflex, melts at 164°, and gives the same reactions as other nitroso-bases. It is decomposed by boiling soda, yielding methylamine and paranitrosoxylenol.

Methylxylylenediamine [$NHMe : Me_2 : NH_2 = 1 : 2 : 5 : 4$], prepared by reducing the preceding componnd with tin and hydrochloric acid, crystallises in almost colourless needles, melts at 83°, and is readily soluble in ether and alcohol, but only sparingly in water. Its salts are colourless, but, like the base itself, they become coloured on exposure to the air. The *hydrochloride* crystallises from alcohol in colourless needles, and in its aqueous solution ferric chloride gives a deep, violet-blue coloration. The *stannochloride* crystallises in colourless needles.

Paranitrosoxylenol [$NOH : Me_2 : O = 1 : 2 : 5 : 4$], crystallises in yellowish prisms, melts at 165°, and is readily soluble in ether and alcohol; it behaves like other nitroso-phenols, and dissolves in ammonia and dilute alkalis yielding red solutions.

Paranitrosoxylidine, $C_8H_{10}N_2O$, obtained by heating nitrosoxylenol with ammonium chloride and ammonium acetate, crystallises from benzene and ether in green needles melting at 169°; it is sparingly soluble in water, and is decomposed by boiling alkalis.

Paraxyloquinonedioxime, $C_8H_{10}N_2O_2$, can be obtained by treating the nitroso-base with hydroxylamine hydrochloride in cold dilute alcoholic solution; it crystallises from boiling alcohol in slender, yellow needles, melts at 254°, and is sparingly soluble in all ordinary solvents except alkalis.

Dinitrosoxylene, $C_8H_8N_2O_2$, prepared by oxidising xyloquinonedioxime with potassium ferricyanide in alkaline solution, is a yellow, sparingly soluble compound melting at about 250°. F. S. K.

Methylorthanisidine. By T. T. Best (*Annalen*, **255**, 176—188).—*Methylorthanisidylnitrosamine*, $OMe{\cdot}C_6H_4{\cdot}NMe{\cdot}NO$, can be obtained by dissolving methylorthanisidine (prepared from orthanisidine by Hepp's method, *Ber.*, **10**, 327) in dilute sulphuric acid, covering the solution with a little ether, and gradually adding an aqueous solution of sodium nitrite, with constant shaking. On evaporating the ethereal solution, the nitrosamine remains as a yellow oil. It gives Liebermann's reaction, and is readily soluble in alcohol and ether, but insoluble in water.

Paranitrosomethylorthanisidine, $OMe{\cdot}C_6H_3(NO){\cdot}NHMe$, is formed when the preceding compound is treated with an alcoholic solution of hydrochloric acid in the cold, and the salt produced decomposed with dilute ammonia. It crystallises in green or steel-blue plates, melts at 110°, and is readily soluble in alcohol, benzene, glacial acetic acid,

ether, and methyl alcohol, but only very sparingly in light petroleum and water. The *hydrochloride*, $C_8H_{10}N_2O_2,HCl$, separates from water and alcohol in long, yellowish-green needles or plates, and is very readily soluble in water, only moderately easily in alcohol, and insoluble in ether. It is decomposed by hot dilute soda, giving methylamine and the sodium compound of nitrosoguaiacol. The *sulphate* crystallises in yellow or brown plates, and is moderately easily soluble in water. The *platinochloride*, *picrate*, and *oxalate* are yellow or brown, sparingly soluble compounds.

When paranitrosomethylorthanisidine is warmed with aniline and aniline hydrochloride, it is converted into azophenine (m. p. 241°) (compare Abstr., 1887, 1105).

Paranitroanisylmethylnitrosamine, $OMe\cdot C_6H_2(NO_2)\cdot NMe\cdot NO$, is obtained when methylorthanisidine or methylorthanisidylnitrosamine sulphate is treated with excess of sodium nitrite in dilute sulphuric acid solution; it crystallises from dilute alcohol in long, yellowish needles, melts at 138°, and is soluble in alcohol, but only moderately easily in ether, and insoluble in water. It gives Liebermann's reaction, and, when treated with alcoholic hydrochloric acid, it is converted into paranitromethylanisidine.

Methoxymethylparaphenylenediamine [$NHMe : NH_2 : OMe = 1 : 4 : 6$] is prepared by reducing paranitrosomethylorthanisidine with tin and concentrated hydrochloric acid and decomposing the resulting crystalline stannochloride with cold soda. It crystallises from light petroleum in long, colourless needles, turns reddish on exposure to the air, and melts at 67—68°; it is readily soluble in water, alcohol, ether, and acids, but rather more sparingly in light petroleum. The *hydrochloride* crystallises from alcohol in colourless needles; its aqueous solution is coloured deep violet or blue on the addition of ferric chloride. The *platinochloride* separates from water in dark-brown crystals.

Paranitrosoguaiacol, $OMe\cdot C_6H_3(NO)\cdot OH$, prepared by boiling paranitrosomethylanisidine hydrochloride with soda, crystallises in needles or prisms, and decomposes at 140—150° with a slight explosion. It is readily soluble in alcohol and ether, but only sparingly in water. When treated with hydroxylamine hydrochloride in alcoholic solution, it is converted into methoxyquinonedioxime (see below). The sodium, potassium, and ammonium derivatives are red, crystalline compounds which decompose with a slight explosion when heated, and are soluble in alcohol.

Paranitrosoanisidine, $OMe\cdot C_6H_3(NO)\cdot NH_2$, is obtained by heating the preceding compound with ammonium acetate and ammonium chloride, with frequent addition of ammonium carbonate. It separates from benzene and ether in green crystals, melts at 107°, and is readily soluble in alcohol, ether, benzene, and acids, but only sparingly in water.

Methoxyquinonedioxime, $OMe\cdot C_6H_3(N\cdot OH)_2$, prepared by treating nitrosoanisidine with hydroxylamine hydrochloride, crystallises from dilute alcohol in small, grey needles, melts at 250° with decomposition, and is soluble in ether and alkalis, but insoluble in water. When treated with a cold alkaline solution of potassium ferricyanide, it is

converted into paradinitrosoanisoïl. This compound, $OMe \cdot C_6H_3(NO)_2$, forms yellow crystals, melts at 94—96° with partial decomposition, and is almost insoluble in all solvents; it is oxidised to paradinitroanisoïl by potassium ferricyanide. F. S. K.

Paramidodiphenylamine. By C. HENCKE (*Annalen*, **255**, 188—195).—Paramidodiphenylamine is best prepared by reducing paranitrosodiphenylamine with alcoholic ammonium sulphide. The *benzylidene*-derivative, $C_{19}H_{16}N_2$, crystallises from alcohol and benzene in greenish plates, melts at 107—109°, and is decomposed by dilute acids and alkalis. The *benzyl*-derivative, $C_{19}H_{18}N_2$, prepared by reducing the preceding compound with sodium and alcohol, crystallises in yellowish plates, and melts at 124°. The *paranitrobenzylidene*-derivative crystallises from benzene in red needles, and is sparingly soluble in ether, alcohol, and light petroleum; it melts at 172°. The corresponding *metanitro*-compound forms yellow plates, melts at 123°, and is more readily soluble in ether and alcohol than the paracompound.

Orthohydroxybenzylideneparamidodiphenylamine, prepared from the amido-base and salicylaldehyde, separates from alcohol in dark yellow crystals, and from hot benzene in brown prisms melting at 120°. Cumaldehyde and the amido-base combine together yielding a compound $C_{22}H_{22}N_2$, which crystallises from alcohol in brown prisms melting at 132°. The condensation-product obtained from furfuraldehyde has the composition $C_{17}H_{14}N_2O$; it separates from alcohol in yellow crystals melting at 129°.

Phthalamidodiphenylamine, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N \cdot C_6H_4 \cdot NHPh$, prepared by heating the amido-base with phthalic acid at 180°, forms green needles, melts at 270°, and is almost insoluble in water, alcohol, ether, benzene, and light petroleum.

The compound $CS(NH \cdot C_6H_4 \cdot NHPh)_2$ is obtained when paramidodiphenylamine is boiled with carbon bisulphide in alcoholic solution; it crystallises from dilute alcohol in colourless needles, melts at 180°, and when boiled with mercuric oxide in alcoholic solution is converted into a yellowish-green, crystalline compound which melts at 117° and has the composition $C_{25}H_{18}N_4S$.

Paramidodiphenylamine combines with quinone yielding a dark red, sparingly soluble compound $C_6H_2O_2(NH \cdot C_6H_4 \cdot NHPh)_2$ [$(NH \cdot)_2 =$ 2 : 3], which melts above 360°.

Phenylquinonediimide, $(C_{12}H_{10}N_2)_n$, is formed when an ethereal solution of paramidodiphenylamine is shaken for a few minutes with finely-divided lead peroxide. It crystallises from methyl alcohol with 3 mols. of the solvent, melts at 208°, and behaves like an indamine. When treated with alcoholic ammonium sulphide at 120°, it is reconverted into the amido-base, and when warmed with aniline and aniline hydrochloride, it yields azophenine and an induline base. F. S. K.

Phenylparatolylamine. By A. REICHOLD (*Annalen*, **255**, 162—168).—*Paranitrosophenyltolylamine*, $C_{13}H_{12}N_2O$, can be easily prepared by dissolving phenylparatolylnitrosamine in alcoholic ether, and

adding alcoholic hydrochloric acid to the ice-cold solution. The hydrochloride, which separates from the solution after some time, is washed with alcoholic ether, and decomposed with alcoholic ammonium sulphide, whereon the base is gradually precipitated in blue prisms or plates. It is moderately easily soluble in alcohol, ether, and chloroform, but more sparingly in benzene, from which it separates in green plates, and very sparingly in hot water and light petroleum. It dissolves in glacial acetic acid with a brown coloration, and in concentrated sulphuric acid yielding a red solution which turns violet on warming. It melts at 163°, and dissolves in dilute alkalis, but is reprecipitated by carbonic anhydride. The salts with acids are decomposed by water. The base is decomposed by boiling soda, yielding paratoluidine and nitrosophenol. The *nitroso*-derivative, $C_{13}H_{11}N_3O_2$, crystallises from ether in green plates, melts at 110° with decomposition, and gives Liebermann's reaction. The *acetyl*-derivative, $C_{15}H_{14}N_2O_2$, forms red crystals melting at 103°.

Benzenediazonitrosophenyltolylamine, $C_{19}H_{18}N_4O$, is obtained when paranitrosophenytolylamine hydrochloride is treated with excess of phenylhydrazine hydrochloride in dilute alcoholic solution. It crystallises from warm alcohol in yellow plates, melts at 125° with decomposition, and explodes when heated quickly. It is decomposed by boiling alcoholic hydrochloric acid with evolution of nitrogen, yielding benzene and nitrosophenyltolylamine.

Methylazophenine [$NC_7H_7 : NPh : (NHPh)_2$ = 1 : 4 : 2 : 5] is formed when the nitroso-base (1 part) is heated at 100° for some hours with aniline (4 parts) and aniline hydrochloride (1 part). The crystalline residue is boiled with dilute alcohol to free it from the induline dye, and then recrystallised from xylene. It forms red plates, melts at 230°, and gives the same reactions as azophenine.

Paramidophenyltolylamine, $C_{13}H_{14}N_2$, prepared by reducing the nitroso-base with alcoholic ammonium sulphide, crystallises in colourless plates, melts at 118°, and is readily soluble in alcohol, ether, and benzene, but more sparingly in light petroleum; it quickly turns violet on exposure to the air. The *sulphate* crystallises in colourless needles, and is only sparingly soluble.

Benzylideneamidophenyltolylamine, $C_{20}H_{18}N_2$, is formed when the amido-base is warmed with benzaldehyde. It crystallises from alcohol in yellow plates, melts at 139°, and turns greenish on exposure to light. It is decomposed by boiling acids, yielding benzaldehyde and the amido-base. The corresponding compound $C_{20}H_{18}N_2O$, obtained in like manner from salicylaldehyde, forms reddish-yellow crystals, melts at 142°, and is moderately easily soluble in alcohol, ether, and benzene.

Paranitrobenzylidenephenyltolylamine, $C_{20}H_{17}N_3O_2$, obtained by boiling an alcoholic solution of the amido-base with paranitrosobenzaldehyde, crystallises in red needles melting at 130°. F. S. K.

Action of Thionyl Chloride on Aromatic Tertiary Amines. By A. MICHAELIS and E. GODCHAUX (*Ber.*, 23, 553—559).—Thiodimethylaniline, $S(C_6H_4 \cdot NMe_2)_2$, is formed, together with dimethylanilinesulphonic chloride, when dimethylaniline is treated with thionyl

chloride (1 mol.) in well-cooled ethereal solution. The ether, which contains the chloride, is decanted, the residual dark, solid product dissolved in dilute hydrochloric acid, the filtered solution rendered strongly alkaline with soda, and distilled with steam to free it from dimethylaniline; the thiodimethylaniline, which remains as a solid, green mass, is then recrystallised from hot alcohol. It forms green needles, melts at 126°, and is readily soluble in ether and hot alcohol (compare Tursini, Abstr., 1884, 1140). The *hydrochloride*, $C_{16}H_{20}N_2S,2HCl$, melts at 176°, is very readily soluble in water, and becomes coloured on exposure to light. The *platinochloride*,

$$C_{16}H_{20}N_2S,H_2PtCl_6 + 2H_2O$$

is yellowish-brown; the *ferrocyanide*, $C_{16}H_{20}N_2S,H_4Fe(CN)_6 + 6H_2O$, is a colourless powder almost insoluble in water.

Dimethylanilinesulphonic acid is obtained when the ethereal solution decanted from the thiodimethylaniline is shaken with dilute hydrochloric acid and then evaporated; it melts at 257°, and is identical with the acid obtained by treating dimethylaniline with fuming sulphuric acid. The *sodium* salt ($+2H_2O$) crystallises from water in long, colourless needles, and is sparingly soluble in soda and insoluble in alcohol.

Thiodiethylaniline can be obtained, together with diethylaniline-sulphonic acid, exactly as described in the case of the corresponding dimethyl-base. It crystallises from alcohol in long, colourless needles, melts at 83°, and is readily soluble in ether and hot alcohol. The *hydrochloride*, $C_{20}H_{28}N_2S,2HCl$, crystallises in long, colourless needles, melts at 94°, and is readily soluble in water. The *sulphate*,

$$C_{20}H_{28}N_2S,H_2SO_4,$$

crystallises in needles melting at 83°; the *ferrocyanide* is colourless. The *picrate*, $C_{20}H_{28}N_2S,C_6H_3N_3O_7$, crystallises from alcohol in small, yellow needles melting at 177°.

Diethylanilinesulphonic acid turns brown at 250°, and melts at 270° with decomposition.

Sodium methylbenzylanilinesulphonate, $C_7H_7 \cdot NMe \cdot C_6H_4 \cdot SO_3Na + 3H_2O$, is obtained when methylbenzylaniline is treated with thionyl chloride in ethereal solution, the product dissolved in hydrochloric acid, and precipitated with soda. It crystallises in plates and melts at 100° in its water of crystallisation, the anhydrous substance melting at 238°; it is readily soluble in water and hot alcohol.

Sodium ethylbenzylanilinesulphonate, $C_7H_7 \cdot NEt \cdot C_6H_4 \cdot SO_3Na + 3H_2O$, prepared in like manner, melts at 222°.

The action of selenyl chloride on aromatic tertiary amines is being investigated, as is also the behaviour of primary and secondary bases.

F. S. K.

Alkylorthophenylenediamines and their Derivatives. By A. HEMPEL (*J. pr. Chem.* [2], 41, 161—178).—*Orthonitroethylaniline*, $NO_2 \cdot C_6H_4 \cdot NHEt$, is best obtained by heating ethyleneorthonitrophenol with ethylamine in alcohol at 140°, evaporating on the water-bath, and distilling the oily residue with steam; the oil is extracted from the distillate by ether, dissolved in strong hydrochloric acid,

filtered, and precipitated by water. It is a red oil which does not crystallise, and decomposes at 95° when distilled; it is slightly soluble in warm water and burns with a sooty, luminous flame.

Orthonitromethylaniline, obtained in like manner, is a red oil which crystallises on cooling in red needles melting at 26—28°, and soluble in much cold water.

Ethylorthophenylenediamine, $NH_2 \cdot C_6H_4 \cdot NHEt$, obtained by reducing orthonitroethylaniline with tin in hydrochloric acid, is a colourless, strongly smelling oil, unstable in light and air, and distilling at 248—249°. Its *platinochloride* was obtained.

Ethylazimidobenzene, $C_6H_4<\substack{NEt \\ N}>N$ (compare Abstr., 1888, 273), is obtained by decomposing ethylorthophenylenediamine (10 grams) with the calculated quantity of sodium nitrite in dilute sulphuric acid, filtering, and extracting the filtrate with ether. It is an odorous, yellow oil boiling at 280—281°, soluble in strong, and warm dilute sulphuric acid, and precipitated unchanged by alkalis.

Acetylethylorthophenylenediamine, $NHEt \cdot C_6H_4 \cdot NHAc$, is precipitated when ethereal solutions of the calculated quantities of ethylorthophenylenediamine and acetic anhydride are mixed together; it forms white crystals becoming brownish-red on exposure to the air, melts at 104°, and is sparingly soluble in most solvents, but freely soluble in dilute acids and in alcohol.

Ethenylethylorthophenylenediamine, $C_6H_4<\substack{NEt \\ N}>CMe$, is formed (1) by mixing acetic anhydride with ethylorthophenylenediamine; (2) by gently warming ethereal solutions of acetic chloride and ethylorthophenylenediamine together, and then evaporating the ether; (3) by reducing orthonitroacetylethylaniline with tin and hydrochloric acid. It crystallises from alcohol in colourless, rhombic tables, melts at 179—180°, and is soluble in ether, dilute acids, and warm water; its *hydrochloride* forms colourless needles soluble in water.

Orthonitronitroso-ethylaniline, $NO_2 \cdot C_6H_4 \cdot NEt \cdot NO$, is obtained by treating orthonitroethylaniline in strong hydrochloric acid with sodium nitrite; it separates as a yellow oil which solidifies on cooling, and crystallises from dilute alcohol in long, yellow needles melting at 30°. It does not give a nitroso-reaction. The action of nitrous anhydride on orthonitroethylaniline in ether produces 1 : 2 : 4-dinitroethylaniline. *Orthonitronitrosomethylaniline*, prepared in like manner forms a red oil which solidifies in pale-yellow needles melting at 36°.

Orthamidophenylethylhydrazine, $NH_2 \cdot C_6H_4 \cdot NEt \cdot NH_2$, is obtained by passing hydrogen sulphide through a solution of orthonitronitroso-ethylaniline (10 grams) in absolute alcohol (300 c.c.) mixed with strong ammonia; a *thiosulphate*, $C_8H_{13}N_3,H_2S_2O_3$, separates from the solution, which, after washing with alcohol and carbon bisulphide, forms colourless crystals smelling of garlic and remarkably soluble in water; the filtrate contains a considerable quantity of the free base, which may be separated by evaporating over the water-bath, adding concentrated hydrochloric acid, filtering, and adding excess of aqueous soda. If ammonium sulphide is substituted for ammonia and

hydrogen sulphide, the hydrazine compound is formed without the thiosulphate. It is a yellowish-red oil smelling of nicotine, and is easily resinified; it decomposes above 100°, giving a yellow vapour which irritates the eyes; it is soluble in ether, alcohol, and dilute acids; it reduces sulphuric acid, evolving sulphurous anhydride. The *hydrochloride* and *platinochloride* are described. *Orthamidophenylmethylhydrazine*, prepared in like manner, is a red oil having much the same properties as the ethyl compound.

Acetylorthamidophenylethylhydrazine, $NHAc\cdot C_6H_4\cdot NEt\cdot NH_2$, formed by the action of acetic chloride on orthamidophenylethylhydrazine dissolved in ether, crystallises from absolute ether in yellow deliquescent needles, melts at 89—91°, and is soluble in alcohol, ether, and dilute acids. Sulphuric acid decomposes it, evolving sulphurous anhydride and nitrogen, and forming acetylethylorthophenylenediamine (see above); this decomposition indicates the presence of a non-substituted hydrazine-group, and settles the position of the acetyl-group. *Acetylorthamidophenylmethylhydrazine*, prepared in like manner, crystallises in yellow needles melting at 129—131°. When it is heated, it loses nitrogen and water forming ethenylethylorthophenylenediamine (see above).

α-Phenotriazine has been already described by Bischler (this vol., 149); it is also produced by the action of phosphoric anhydride on acetylorthamidophenylmethylhydrazine. The two substances are mixed together, left in a desiccator for some days, and then in the air until all the phosphoric anhydride has been converted into phosphoric acid; the liquid thus obtained is neutralised with sodium carbonate and extracted with ether, which dissolves the α-phenotriazine.

α-Methylphenotetrazine, $C_6H_4{<}\begin{array}{l}NH-N\\ \quad\;\; \| \\ NMe\cdot N\end{array}$, is obtained when the calculated quantity of sodium nitrite is added to a strong solution of orthamidophenylmethylhydrazine in dilute hydrochloric acid kept cold. After the action, soda is added, and the mixture shaken with ether, which extracts the tetrazine and, on evaporation, leaves it as a red oil which solidifies on cooling, and forms colourless, pearly leaflets when dried on a plate of gypsum. It melts at 62° and is soluble in ether, benzene, warm alcohol, and warm petroleum; it is precipitated in yellow flocks from its solution in mineral acids. When heated with strong nitric acid at 80—100° and then cooled, it yields yellow prisms and needles of the composition $C_5H_4O_6N_4$, melting at 127°; this substance is still under investigation. A. G. B.

Paranitrosodiphenylmetaphenylenediamine. By O. FISCHER and E. HEPP (*Annalen*, **255**, 144—147; compare Ikuta, Abstr., 1888, 467).—*Paranitrosodiphenylmetaphenylenediamine*, $\overset{5}{N}HPh\cdot C_6H_3{<}\begin{array}{l}\overset{1}{N}HPh\\ \;| \\ \underset{4}{N}\end{array}{>}O$, can be obtained by treating diphenylmetaphenylenediamine with amyl nitrite and hydrochloric acid in alcoholic ethereal solution, and decomposing the salt thus produced with

ammonia. It crystallises from benzene in brownish-red prisms with a blue reflex, and is insoluble in alkalis. The *hydrochloride*, $C_{18}H_{15}N_3O,HCl$, crystallises in small, red needles.

Amidodiphenylmetaphenylenediamine $[(NHPh)_2 : NH_2 = 1 : 3 : 4]$, prepared by reducing the preceding compound with tin and hydrochloric acid in alcoholic solution, and decomposing the resulting salt with alkalis, crystallises from a mixture of benzene and light petroleum in almost colourless needles melting at 107°.

Azophenine (Abstr., 1887, 1105) is formed when the nitroso-compound is heated at 110° with aniline and aniline hydrochloride.

Paranitrosomethyldiphenylamine and *paranitrosobenzylaniline* have been prepared from methyldiphenylamine and benzylaniline respectively, and will be described in a later paper.

When nitroso-α-naphthylamine is heated with α-naphthylamine and α-naphthylamine hydrochloride, it is converted into α-β-naphthazine melting at 275° (compare Abstr., 1887, 1114). F. S. K.

Action of Aniline on Benzene Hexachloride. By P. Mohr (*Monatsh.*, **11**, 22—27).—When benzene hexachloride (1 mol.) is heated with aniline (4 mols.) in a reflux apparatus, only aniline hydrochloride and trichlorobenzene are formed; but when the hexachloride (1 mol.) is heated with a large excess of aniline (12 mols.) in a sealed tube at 130° for 4—6 hours, a brownish-yellow, crystalline mass, which contains *triphenylamidobenzene*, $C_6H_3(NHPh)_3$, is formed. The new compound crystallises in hexagonal or rhombic, microscopic plates of a golden-yellow colour, which turn brown at 238° and melt at 242°. It is readily soluble in chloroform, benzene, toluene and carbon bisulphide, slightly soluble in ether and light petroleum, but insoluble in water or alcohol. The author supposes it to be formed by the action of trichlorobenzene, produced by the decomposition of the hexachloride, on aniline; this mode of formation explains the very small yield (0·5 per cent. of the hexachloride used) obtained. G. T. M.

Hydroxyazo- and Amidoazo-compounds. By H. Goldschmidt and Y. Rosell (*Ber.*, **23**, 487—508).—With a view of ascertaining the constitution of certain hydroxyazo- and amidoazo-compounds, the authors have studied the behaviour of several substances of this nature with phenylcarbimide (compare this vol., p. 498) and with benzaldehyde (compare Meldola, Trans., 1890, 328).

Carbanilidohydroxyazobenzene, $C_{19}H_{15}N_3O_2$, is formed when hydroxyazobenzene (1 mol.) is heated at 170° with phenylcarbimide (1 mol.) and a little benzene. It crystallises from benzene in orange needles, melts at 149°, and is readily soluble in alcohol, ether, and benzene, but insoluble in alkalis. It is very readily decomposed by warm alcoholic potash, yielding hydroxyazobenzene, aniline, and carbonic anhydride.

Dicarbanilidohydrazobenzene, NHPh·CO·NPh·NPh·CO·NHPh, is obtained when hydrazobenzene (1 mol.) is heated at 150° with phenylcarbimide (2 mols.) and a little benzene. It melts at 218—220°, is insoluble in all ordinary solvents, and is not decomposed on prolonged

boiling with alcoholic potash; it is not acted on by concentrated hydrochloric acid at 150°, but at 200° it is decomposed into aniline, carbonic anhydride, and benzidine hydrochloride. The great difference in the behaviour of these two carbanilido-compounds with alcoholic potash shows a dissimilarity in constitution: as the dicarbanilido-compound has probably the constitution assigned to it above, that of the monocarbanilido-compound is probably represented by the formula $NHPh{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}N_2Ph$, in which case hydroxyazobenzene would be a true hydroxy-derivative, and not the hydrazone of a qninone.

Carbanilidohydroxyhydrazobenzene, $C_{19}H_{17}N_3O_2$, can be prepared by reducing the corresponding hydroxyazo-compound with zinc-dust in warm glacial acetic acid solution. It crystallises from benzene in colourless needles, melts at 155°, and rapidly oxidises on exposure to the air. It is insoluble in alkalis, but when warmed with alcoholic potash, it is immediately decomposed into aniline and hydroxyhydrazobenzene; the last-named compound is, however, immediately oxidised, and on adding water hydroxyazobenzene is precipitated. This behaviour seems to show that the constitution of the carbanilido-compound is $NHPh{\cdot}NH{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}NHPh$.

The compound $NPh{:}N{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}NH{\cdot}C_{10}H_7$ is obtained when hydroxyazobenzene is treated with α-naphthylcarbimide as described in the case of the phenyl-derivative. It melts at 149°. The corresponding *hydrazo*-componnd, $NHPh{\cdot}NH{\cdot}C_6H_4{\cdot}O{\cdot}CO{\cdot}NH{\cdot}C_{10}H_7$, obtained by treating the azo-compound with zinc-dust and glacial acetic acid, crystallises from benzene in colourless needles, melts at 155°, and is only sparingly soluble in ether.

Carbanilidohydroxyhydrazobenzene (see above) combines with phenylcarbimide yielding a compound $C_{33}H_{27}N_5O_4$, probably *tricarbanilidohydroxyhydrazobenzene*, which separates from alcohol as a colourless, crystalline powder, melts at 215—218°, and is very sparingly soluble in benzene. It dissolves in boiling alcoholic potash yielding a dark-green solution which contains aniline, diphenylcarbamide, an amidophenol, and a phenol-like substance melting at 206—208°.

Carbanilidohydroxyhydrazobenzene combines with acetic anhydride yielding a thick oil. When heated alone at about 150°, it is converted into an isomeride, which crystallises from alcohol in colourless needles melting at 218—220°. This isomeride seems to be unchanged by stannous chloride and hydrochloric acid, but it is decomposed by concentrated hydrochloric acid at 150°, yielding aniline, an amidophenol-like substance, and carbonic anhydride.

Benzeneazoparacresol and benzeneazo-β-naphthol do not combine with phenylcarbimide even at 220°, a fact which, in the authors' opinion, tends to show that both compounds are hydrazones of orthoquinones. This opinion is based on the fact that, although benzylidenehydrazone combines with phenylcarbimide, benzeneazoacetone, which has a constitution somewhat analogous to that of the hydrazone of an orthoquinone, does not do so.

Carbanilidophenoldisazobenzene, $NHPh{\cdot}CO{\cdot}O{\cdot}C_6H_3(N_2Ph)_2$ is formed when phenoldisazobenzene [$OH : (N_2Ph)_2 = 1 : 2 : 4$] is heated with

phenylcarbimide and a little benzene at 170°. It crystallises from hot benzene in small, yellow needles, melts at 133—135°, and is readily soluble in alcohol and ether. When reduced with zinc-dust and glacial acetic acid, it gives a colourless hydrazo-compound.

Amidoazobenzene and benzeneazo-β-naphthylamine do not combine with carbodiphenylimide or with carboparaditolylimide; this fact tends to show that both these azo-compounds are imido- and not amido-derivatives.

Carbanilidoamidoazobenzene (*benzeneazodiphenylcarbamide*),

$$NHPh\cdot CO\cdot NH\cdot C_6H_4\cdot N_2Ph,$$

is obtained when a solution of paramidoazobenzene (1 mol.) is treated with phenylcarbimide in the cold. It crystallises from hot alcohol in golden flakes, melts at 216°, and is almost insoluble in benzene, but readily soluble in hot alcohol. It does not combine with phenylcarbimide, and when reduced with tin and hydrochloric acid, it yields aniline and a colourless, crystalline compound, probably paramidodiphenylcarbamide.

Carbanilidoamidoazotoluene, $C_{21}H_{20}N_4O$, obtained from orthamidoazotoluene in like manner, crystallises in golden needles, melts at 219°, and is almost insoluble in benzene and only moderately easily soluble in hot alcohol. On reduction with stannous chloride and hydrochloric acid, it yields a colourless compound, probably amidotolylphenylcarbamide, which melts at 195°.

Carbanilidobenzeneazo-β-naphthylamine, $C_{23}H_{18}N_4O$, is formed when benzeneazo-β-naphthylamine is heated at 125° with phenylcarbimide and a little benzene. It crystallises from hot alcohol or benzene in orange-red needles melting at 205°. When reduced with stannous chloride and hydrochloric acid in alcoholic solution, it is converted into *amidonaphthylphenylcarbamide*, $NH_2\cdot C_{10}H_6\cdot NH\cdot CO\cdot NHPh$; this compound crystallises in small needles and melts at 290°.

When benzeneazo-β-naphthylamine is heated with phenylcarbimide (2 mols.) and benzene at 150°, the carbanilido-compound (m. p. 205°) described above, diphenylcarbamide, and a yellow, sparingly soluble, crystalline compound of the composition $C_{17}H_{11}N_3O$ are formed. The last-named crystallises from ethyl acetate in yellow needles, melts at 252°, and is only sparingly soluble in benzene; it dissolves in concentrated sulphuric acid with a red coloration, and in hydrochloric acid yielding a yellow solution, from which it is precipitated unchanged on adding ammonia. It is completely decomposed by concentrated hydrochloric acid at 160°, yielding a phenol and β-naphthylamine. The constitution of this compound is probably $C_{10}H_6{<}\begin{matrix}N\cdot CO\\ \mid\\ N\cdot NPh\end{matrix}$.

Its formation is best explained by assuming that benzeneazo-β-naphthylamine has the constitution $NH\!:\!C_{10}H_6\!:\!N\cdot NHPh$. Orthamidoazotoluene is probably analogously constituted.

Benzylideneorthamidoazotoluene, $C_{21}H_{19}N_3$, is obtained when orthamidoazotoluene is treated with excess of benzaldehyde in the cold; it crystallises from alcohol in colourless needles, and melts at 220°.

Benzeneazobenzylidene-β-naphthylamine, $C_{23}H_{17}N_3$, is formed when benzeneazo-β-naphthylamine is heated with benzaldehyde at 140°. It

separates from boiling alcohol as a microcrystalline powder, melts at 193°, and is only sparingly soluble in benzene and ether. It is not decomposed by boiling concentrated hydrochloric acid, and when heated therewith at 150°, it is simply converted into the *hydrochloride*, $C_{23}H_{17}N_3,HCl$, which separates from alcohol in colourless crystals melting at 220°. This behaviour seems to show that the constitution of the base is $C_{10}H_6 \lessgtr \begin{matrix} NH\cdot CHPh \\ | \\ N—NPh \end{matrix}$; benzylideneorthamidoazotoluene has probably an analogous constitution. F. S. K.

Inorganic Derivatives of Phenylhydrazine. By A. MICHAELIS and J. RUHL (*Ber.*, **23**, 474—477).—It has been shown by E. Fischer (*Annalen*, **190**, 124) that sulphurous anhydride and phenylhydrazine combine together forming two different additive compounds, N_2H_3Ph,SO_2 and $2N_2H_3Ph,SO_2$. The authors have confirmed these results, and show that the latter compound is readily prepared by saturating an alcoholic solution of phenylhydrazine with sulphurous anhydride, and allowing the clear liquid to evaporate in the air at the ordinary temperature. It crystallises in beautiful, white tablets which sinter together at 70°, blacken without melting at a higher temperature, and are readily soluble in alcohol and water, insoluble in ether and benzene.

If sulphurous anhydride be passed into a cold benzene solution of phenylhydrazine, the additive product N_2H_3Ph,SO_2 separates, but on heating gradually, it loses water, forming *thionylphenylhydrazone*, $NHPh\cdot N\dot{:}SO$. This compound, which may also be directly prepared by heating the benzene solution to 75°, and then passing in sulphurous anhydride, is identical with the compound obtained by the action of thionyl chloride on phenylhydrazine (Abstr., 1889, 1163). To isolate it, that portion which separates on cooling is filtered off, the filtrate shaken with dilute acetic acid until all the phenylhydrazine is removed, the benzene solution evaporated, and the combined portions of the hydrazone recrystallised from boiling alcohol.

If sulphurous anhydride is passed for too long a time, and the solution heated to boiling, the chief product is phenyl bisulphide, S_2Ph_2, which may be readily prepared in this manner, and separated from thionylphenylhydrazone by dilute aqueous soda. The careful separation of phenylhydrazine, mentioned above, is necessitated by the fact that this reacts with thionylphenylhydrazone to form phenyl bisulphide.

Thionylparatolylhydrazone, $C_7H_7\cdot N_2H\dot{:}SO$, is prepared in a similar manner from paratolylhydrazine, and resembles thionylphenylhydrazone in all its properties; by alkalis, it is converted into sodium sulphate and paratolylhydrazine. Orthotolylhydrazine does not react with sulphurous anhydride so readily, and yields an oily compound which has a peculiar aromatic odour, and is decomposed by alkalis in the same way as the para-compound. The secondary hydrazines are without action on sulphurous anhydride.

These results yield additional evidence of the similarity existing between sulphurous acid and the aldehydes. H. G. C.

Phenylammeline and Phenylisocyanuric Acid. By A. SMOLKA and A. FRIEDREICH (*Monatsh.*, **11**, 1—14; compare Abstr., 1889, 114 and 951).—*Phenylammeline*, $C_3H_4PhN_5O$, may be prepared by heating together molecular proportions of phenylbiguanide hydrochloride and carbamide for half an hour at 150—160°, or by heating together dicyanodiamide and monophenylcarbamide in molecular proportions at 150—160°, but not by the interaction of biguanide hydrochloride and monophenylcarbamide, which gives rise to unsubstituted ammeline and aniline. Phenylammeline forms a white powder insoluble in water, but soluble in dilute mineral and acetic acids and in the alkalis. Boiling alcohol slightly dissolves the substance, which, on cooling the solution, crystallises out in microscopic needles. The hydrochloride, $C_3H_4PhN_5O,HCl$, crystallises in bundles of radiating needles fairly soluble in water, but insoluble in alcohol; the platinochloride is soluble in alcohol but decomposed by water; the sulphate, $C_3H_4PhN_5O,H_2SO_4 + \frac{1}{2}H_2O$, is readily soluble in water, and melts with decomposition at 125—130°.

Phenylisocyanuric acid, $C_3H_2PhN_3O_3$, is formed by heating phenylammeline with concentrated hydrochloric acid in sealed tubes for 4—5 hours at 150°. It crystallises in anhydrous, lustrous needles, is scarcely soluble in cold water, slightly soluble in boiling water and in boiling alcohol, and is dissolved readily by ammonia and the fixed alkalis. It melts with partial sublimation at above 240°, and on heating with concentrated hydrochloric acid at 200° for five hours, it is resolved into aniline, carbonic anhydride, and ammonia. The barium salt crystallises with $3H_2O$; the copper, silver, and sodium salts are described.

The authors, contrary to their earlier views (*loc. cit.*), now conclude that the constitution of ammeline must be represented by a closed chain, and that the formation of phenylammeline and phenylisocyanuric acid, above mentioned, points to their having the constitutions respectively represented by the formulæ

$$NPh<\begin{matrix}C(NH)\cdot NH\\CO——NH\end{matrix}>C:NH \text{ and } NPh<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO.$$

G. T. M.

Dihydroxyphosphinic and Hydroxyphosphinous Acids. By J. VILLE (*Compt. rend.*, **110**, 348—350).—The formation of dihydroxyphosphinic acids by the combination of aldehydes with hypophosphorous acid (Abstr., 1889, p. 1134) is accompanied by the formation of hydroxyphosphinous acids. If the mother liquor from dihydroxybenzoylphosphinic acid is mixed with normal lead acetate, a white precipitate is thrown down, and if this is treated with hydrogen sulphide and the filtrate concentrated, the hydroxyphosphinous acid is obtained in thin lamellæ soluble in water, alcohol, and ether. It is a strong acid, decomposing carbonates, and dissolving zinc and iron with evolution of hydrogen. It melts at about 90°, and decomposes at 140° with liberation of benzaldehyde; if more strongly heated, it evolves hydrogen phosphide, and leaves a bulky, carbonaceous residue containing metaphosphoric acid. Hydroxybenzoylphosphinous acid gives the general reactions of phosphorous acid; it has no action on

copper sulphate, reduces silver nitrate slowly in the cold and rapidly on heating, and precipitates crystalline mercurous chloride from a solution of mercuric chloride. The acid contains the elements of a molecule of benzaldehyde and a molecule of hypophosphorous acid, and yields a barium salt $(OH{\cdot}CHPh{\cdot}PHO{\cdot}O)_2Ba + \frac{1}{2}H_2O$, crystallising in small nodules which become anhydrous at 105—110°, and an acetyl-derivative, *acetobenzoylphosphinous acid*, $OAc{\cdot}CHPh{\cdot}PHO{\cdot}OH$, a yellowish, resinous compound, easily soluble in ether, alcohol, and chloroform, but insoluble in ether and benzene. This acetyl-derivative is almost insoluble in water, by which it is resolved into acetic acid and hydroxybenzoylphosphinous acid. A similar change is produced more rapidly by potassium hydroxide.

Dihydroxybenzoylphosphinic acid and hydroxybenzoylphosphinous acid are typical of the two series of acids, which may be represented respectively by the generic formulæ $PO(CHR{\cdot}OH)_2{\cdot}OH$ and $OH{\cdot}CHR{\cdot}PHO{\cdot}OH$.

The proportion of hydroxyphosphinous acid formed in the reaction increases with the proportion of hypophosphorous acid present.

C. H. B.

Isomeric Dichlorobenzaldehydes, and the Naphthols derived therefrom. By E. SCHWECHTEN (*Chem. Centr.*, 1890, i, 217—218; from *Zeit. Naturwiss.*, **62**, 239—268).—With the object of obtaining chlorinated naphthalenes, in which the relative position of the chlorine-atom in the closed chain is known, the author has prepared the four dichloro-derivatives, $C_{10}H_6Cl_2$ [1 : 2; 2 : 3; 1 : 3; and 1 : 4].

The method employed was to first prepare dichlorobenzaldehydes, to convert these by condensation with succinic acid into dichlorophenolparaconic acids, from which the corresponding dichlorophenylisocrotonic acids and dichloro-α-naphthols of definite constitution were obtained.

The dichlorobenzaldehydes were prepared from dichlorotoluenes, which were converted into dichlorobenzyl chlorides, and these into the aldehydes.

The following compounds were prepared. Orthoparadichlorotoluene, $C_6H_3Cl_2Me$ [$Me : Cl_2 = 1 : 2 : 4$], a colourless liquid boiling at 196—197·5°. Orthodichlorotoluene [$Me : Cl_2 = 1 : 3 : 4$] boils at 205—208°. *Orthoparadichlorobenzaldehyde*, $C_6H_3Cl_2{\cdot}CHO$ [$CHO : Cl_2 = 1 : 2 : 4$], boils at 231—245°, melts at 70—71°, and crystallises in snow-white prisms. *Paradichlorobenzaldehyde* [$CHO : Cl_2 = 1 : 2 : 5$], melts at 57—58°, crystallises in needles from alcohol; by oxidation it is converted into dichlorobenzoic acid (m. p. 152—153°), and this into dichlorobenzene (m. p. 53—54), which determine its constitution. *Orthodichlorobenzaldehyde* [$CHO : Cl_2 = 1 : 3 : 4$] melts at 43—44°, and boils at 247—248°. From these dichloroaldehydes the following compounds are obtained by heating with potassium acetate and succinic anhydride at 130—140°. *Orthoparadichlorophenylparaconic acid*, $C_{11}H_8Cl_2O_4$, white lustrous plates melting at 164·5—165·5°. Strong sulphuric acid colours it brown, and it has a bitter taste. *Paradichlorophenylparaconic acid*, $C_{11}H_8Cl_2O_4 + H_2O$, crystallises in white, silky plates, melts at 197—198°, and is turned brown by strong sulphuric acid. *Orthodichlorophenylparaconic acid* melts at 136—137°,

crystallises in snow-white needles, and is coloured dark-brown by concentrated sulphuric acid. By careful heating, the dichlorophenylparaconic acids are converted, with separation of carbonic anhydride, into dichlorophenylisocrotonic acids, from which the corresponding dichloro-α-naphthols are formed at a higher temperature. These compounds are: *parachlorophenylisocrotonic acid*, $C_{10}H_9ClO_2$, melting at 108—109°, from which R. Kirchoff's chloronaphthol melting at 123° is obtained; *orthoparadichlorophenylisocrotonic acid*, white prisms, melting at 120—121°, from which the dichloronaphthol [OH : Cl_2 = 1 : 2′ : 4′] melting at 132° is obtained. This crystallises in light-yellow prisms, and yields an intensely purple-coloured liquid with an alkaline solution of 1 : 4-diazonaphthalenesulphonic acid. *Paradichlorophenylisocrotonic acid* melts at 148—149°, crystallises in white prisms, and is converted into *dichloronaphthol* [OH : Cl_2 = 1 : 1′ : 4′], which is crystalline and melts at 114—115°; with 1 : 4-diazonaphthalenesulphonic acid, it yields a deep violet-coloured liquid. *Orthodichlorophenylisocrotonic acid* melts at 63—64°, and crystallises in white needles. From the orthodichlorophenylparaconic acid, the two dichloronaphthols, OH : Cl_2 = 1 : 2′ : 3 and 1 : 1′ : 2′, might be formed, and, indeed, the author obtained two compounds melting respectively at 149—150° and 83—84°, which also differed from each other in solubility, colour reactions, &c. From these naphthols the corresponding dichloronaphthylamines and dichloronaphthalenes were obtained by heating with ammonia at 300°, and diazotising the amines. *Dichloro-naphthylamine* [1 : 2′ : 4′] crystallises in needles which melt at 116—117°; it yields Cleve's 2 : 3-dichloronaphthalene melting at 60—61°. Dichloronaphthylamine [1 : 1′ : 4′] melts at 68—69°.

J. W. L.

Isocinnamic Acid. By C. LIEBERMANN (*Ber.*, **23**, 512—516; compare this vol., p. 494).—Pure cinnamic acid is precipitated when isocinnamic acid is dissolved in concentrated sulphuric acid (5—6 parts) at 50°, the solution kept for about 15 minutes, and then poured into water.

Isocinnamic acid is also converted into cinnamic acid when it is boiled for 4—5 hours with iodine (2 parts) in carbon bisulphide solution; even at the ordinary temperature this change takes place, but very much more slowly.

Acetic anhydride at 220° converts isocinnamic acid into an anhydride which behaves like that of cinnamic acid, and yields cinnamic acid when treated with sodium carbonate.

Methyl cinnamate is obtained when a solution of isocinnamic acid in methyl alcohol is saturated with hydrogen chloride and kept for some time.

When isocinnamic acid is heated with water at 260°, it is almost completely converted into cinnamene and cinnamic acid; no compound corresponding with truxillic acid is formed.

Although many of the reactions of isocinnamic acid might be explained by assuming that it is the lactone of β-phenyllactic acid, $CHPh{\cdot}CH{<}^{CH_2}_{-O-}{>}CO$, it shows in many respects the distinctive

characters of an acid; that it is not identical with the lactone of β-phenyllactic acid was also proved by direct comparison of its barium salt with that of this lactic acid, and by direct comparison of the two acids.

The view that isocinnamic and cinnamic acids are stereochemically isomeric (*loc. cit.*) is also borne out by the results of determinations, made by Ostwald, of the electrical conductivity of isocinnamic acid.

Isocinnamic acid is not formed in the synthetical preparation of cinnamic acid from benzaldehyde. F. S. K.

Phenylparaconic Acid. By R. FITTIG and P. RÖDERS (*Annalen*, **255**, 142—144; compare Abstr., 1883, 473).—Phenylparaconic acid separates from water in crystals which have the composition $4C_{11}H_{10}O_4 + H_2O$, melt at 99°, and lose their water at 90—100°. The anhydrous substance melts at 121°, but when it has once been liquefied, it melts at 106°; if a particle of a crystal which melts at 121° is brought into contact with some of the liquefied anhydrous compound (the temperature of which may be as high as 115°), the whole gradually solidifies and does not melt until the temperature rises to 121°; after cooling, it melts again at 106°. F. S. K.

Amido-acids. By O. REBUFATT (*Gazzetta*, **19**, 38—58).—*Plöchl's benzoylimidocoumarin*, $C_{16}H_{11}O_3N$ (m. p. 170°), is obtained when sodium hippurate (30 grams), salicylaldehyde (20 grams), and acetic anhydride (70 grams) are heated for half an hour in a reflux apparatus, the product treated with boiling water, and the precipitate crystallised from benzene (Abstr., 1885, 898).

A compound isomeric with the above is prepared by gently heating the same quantities of the reagents until the hippurate commences to dissolve, withdrawing the source of heat and allowing the reaction to go on by itself. The product is then poured into water, and the yellow mass which separates is pressed between filter-paper, washed with alcohol, dried, powdered, and allowed to digest with a cold 5 per cent. solution of potash for one or two days, so as to dissolve the benzoylimidocoumarin. The insoluble residue is collected, washed, dried, and crystallised from acetone, the crystals are again left for a day or two in a 5 per cent. potash solution, and the undissolved portion is washed, and recrystallised once or twice from toluene and finally from acetone. This isomeride forms thick, yellow prisms with a brilliant lustre, melts at 154—155°, and is readily soluble in chloroform, benzene, and toluene, moderately so in warm acetone, but only sparingly in alcohol and acetic acid.

Contrary to Plöchl's statements, it was found that both these isomerides could be converted into acid compounds. Benzoylimidocoumarin (melting at 170°) dissolves in dilute alkaline solutions in the cold, and is reprecipitated unchanged by acids. A concentrated solution of potash (50 per cent.) dissolves a considerable proportion in the cold, without evolution of ammonia; and if the potash is not in excess, crystalline crusts of a *potassium-derivative*, $C_{16}H_{11}O_3N$ +

2KOH, are deposited after one or two days. This compound is decomposed by water, benzoylimidocoumarin being re-formed. If it is left in the mother liquor, however, until the latter has a distinct ammoniacal odour, on dilution and acidification with hydrochloric acid, an acid compound, $C_{16}H_{13}O_4N$, is precipitated. The isomeride melting at 154° is gradually converted into the same compound by a hot 10 to 20 per cent. solution of potash or by a cold 50 per cent. solution.

The acid thus produced may be purified by washing it with petroleum. It crystallises from dilute alcohol in large, colourless tables which melt at 195° with effervescence. It is readily soluble in alcohol, even when dilute, but only very sparingly in chloroform, it is insoluble in ether; it dissolves in solutions of alkaline carbonates with expulsion of carbonic anhydride. It is gradually converted into benzoylimidocoumarin (m. p. 170°) by the action of acetic chloride in the cold, but if it is very gradually dissolved in boiling acetic chloride, the solvent distilled off, and the residue washed with water and recrystallised from acetone, the isomeride melting at 154° is obtained in a state of great purity.

Another isomeride, or perhaps polymeride, of benzoylimidocoumarin may be obtained by adding acetic chloride (50 grams) to the acid (10 grams), suspended in benzene (100 grams), boiling for seven hours in a reflux apparatus, filtering the benzene solution, then washing it with water, drying over calcium chloride, and fractionally distilling; on cooling the residual solution, it deposits lustrous, orange-yellow scales which, after recrystallisation from alcohol, have the composition $C_{16}H_{11}O_3N$. This substance is very unstable and difficult to purify; it melts at 181—182° with effervescence; when it has once been melted and resolidified, the melting point is lowered to 165°; it is readily soluble in benzene, chloroform, acetone, and acetic acid, forming deep-orange coloured solutions; alcohol converts it into benzoylimidocoumarin (m. p. 170°); when boiled with a solution of sodium carbonate, it produces a characteristic cherry-red coloration and dissolves with effervescence; on acidifying the solution, the acid $C_{16}H_{13}O_4N$ is precipitated. The author considers that the first product of condensation between salicylaldehyde and hippuric acid is the acid $C_{16}H_{13}O_4N$, which is largely converted by the excess of acetic anhydride into a mixture of the three isomeric compounds, the relative proportions of which have been found within certain limits to depend only on the quantity of acetic anhydride present. The isomeride melting at 181° cannot be separated from this mixture, but its presence may be shown by the coloration it imparts to a solution of sodium carbonate.

The "anhydride," $C_{32}H_{24}N_2O_7$ (melting at 160°), obtained by Plöchl by the prolonged action of hippuric acid, salicylaldehyde, and acetic anhydride, has no independent existence; it is merely impure benzoylimidocoumarin (m. p. 170°).

A *bromine-derivative* of benzoylimidocoumarin, $C_{16}H_{11}O_3NBr_2$, is obtained by treating its concentrated chloroform solution with excess of a concentrated solution of bromine in chloroform; the new compound separates out in crimson flakes which give off bromine when

exposed to the air. It may be crystallised from a solution of bromine in chloroform. The alkalis convert it into benzoylimidocoumarin.

The isomeride melting at 154° is not attacked by boiling acetic chloride, and forms substitution-derivatives with bromine, but no additive products; by prolonged boiling with alcohol (1 part) and water (3 parts), it is converted into the acid $C_{16}H_{13}O_4N$.

When benzaldehyde and hippuric acid in molecular proportion are treated with excess of acetic anhydride, the product is a mixture of Plöchl's yellow anhydride (m. p. 164), with a little of the substance melting at 225°, regarded by Plöchl as α-benzoylimidocinnamic acid (Abstr., 1884, 1348).

The anhydride is readily soluble in acetone, chloroform, and benzene; it is slowly dissolved in the cold by dilute solutions of the alkalis, and converted into the acid, which again yields the anhydride and an odorous oil on distillation.

After crystallisation from alcohol and acetone, the anhydride has a neutral reaction, melts at 159°, and has the composition $C_{16}H_{11}O_2N$ (not $C_{32}H_{24}O_5N_2$, as stated by Plöchl). It resembles in all respects the yellow isomeride of benzoylimidocoumarin (m. p. 154°), and, like the latter, is formed from the corresponding acid by the abstraction of 1 mol. H_2O.

The condensation of hippuric acid with aldehydes, therefore, results in the formation of unsaturated amido-acids, which, by losing a molecule of water, give rise to a series of yellow compounds, from which the acids are reproduced by the action of alkalis. The constitution of this new class of compounds and of the acids derived from them would be fixed, if the presence of an atom of imide hydrogen in the acid were proved to be necessary for the formation of the yellow compounds. Evidence of this is afforded by the non-formation of any homologous yellow compound by acetylphenylamidoacetic acid, $NPhAc\cdot CH_2\cdot COOH$.

This acid was prepared by heating phenylglycine (8 grams), acetic anhydride (10 grams), and benzene (100 grams) for seven hours. It crystallises from water in nacreous laminæ, and melts at 190—191°. When the sodium salt of this acid is treated with salicylaldehyde and acetic anhydride, &c., as before, the precipitate thrown down by water crystallises from a mixture of alcohol and ether in small, colourless prisms, melts at 155—156°, and has the composition $C_{17}H_{15}O_3N$. It is insoluble in solutions of the alkaline carbonates, but dissolves in solutions of the hydrates, and is reprecipitated unchanged by acids. This compound is evidently *acetylphenyl-α-amidocoumarin*,

$$O<\begin{matrix}C_6H_4\cdot CH \\ \| \\ -CO\cdot C\cdot NPhAc\end{matrix}.$$

It appears that the acids formed by the condensation of hippuric acid with salicylic and benzoic aldehydes are likewise amido-acids, namely, benzoylamido-orthocoumaric and -cinnamic acids. The substance regarded by Plöchl as benzoylimidocoumarin is probably benzoylamidocoumarin, as is indicated by the existence of the potash- and bromine-derivatives.

The yellow compounds are respectively the α-benzoyllactimide of cinnamic acid, $CO<\begin{matrix}NBz\\ |\\ C:CHPh\end{matrix}$ (m. p. 159°), and the α-benzoyllactimide of coumaric acid, $CO<\begin{matrix}NBz\\ |\\ C\cdot CH\cdot C_6H_4\cdot OH\end{matrix}$ (m. p. 154°). S. B. A. A.

Thiocoumarins and their Behaviour towards Hydroxylamine and Phenylhydrazine. By F. ALDRINGEN (*Chem. Centr.*, 1890, i, 119—120).—α-Methylcoumarin, when heated with phosphorus pentasulphide at 120°, is converted into *thio-α-methylcoumarin*, $C_6H_4<\begin{matrix}O-CS\\ \quad\ |\\ CH:CMe\end{matrix}$, melting at 122°. It is reconverted into α-methylcoumarin by heating with hydrochloric acid, hydrogen sulphide being evolved. With hydroxylamine hydrochloride in alcohol and sodium carbonate, *α-methylcoumaroxime*, $C_6H_4<\begin{matrix}O-C:NOH\\ \quad\ |\\ CH:CMe\end{matrix}$, is formed. The latter is decomposed by boiling with aqueous potash, and does not give a brownish-red coloration with ferric chloride. *α-Methylcoumaroxime acetate* melts at 56°. Phenylhydrazine reacts with thiomethylcoumarin, *α-methylcoumarphenylhydrazide*, $C_6H_4<\begin{matrix}O-C:N\cdot NHPh\\ \quad\ |\\ CH:CMe\end{matrix}$, melting at 116°, being formed.

Thio-α-ethylcoumarin, melting at 93—94°, is prepared from ethylcoumarin, as also are *α-ethylcoumaroxime*, melting at 157°; *ethylcoumaroxime acetate*, melting at 61°; and *α-ethylcoumarphenylhydrazide*, melting at 115°. *Thio-α-isopropylcoumarin* melts at 81°, *α-isopropylcoumaroxime* at 170—171°, the *acetate* of the latter at 85°, and the *hydrazide* at 112°.

With umbelliferone and phosphorus pentasulphide, no crystallisable substance could be obtained, but from umbelliferone methyl ether, *thioumbelliferone methyl ether*, melting at 114°, is obtained. *Oximidoumbelliferone methyl ether* melts at 138°, the *phenylhydrazide* at 115°.

J. W. L.

Nitrobenzil and its Isomeric Dioximes. By J. HAUSMANN (*Ber.*, **23**, 531—534).—*Nitrobenzil*, $C_{14}H_9NO_4$, is best prepared by gradually adding benzoïn (10 grams) to cold nitric acid of sp. gr. 1·52 (15 c.c.), the temperature being kept below 25°; the solution is kept for about 15 minutes, then poured into cold water, the semisolid precipitate separated and boiled with concentrated nitric acid (75 c.c.) until the whole dissolves. The nitro-compound, which separates from the solution on cooling, is spread on a porous plate and recrystallised from hot alcohol. It forms small, yellow needles or plates, melts at 141—142°, and is readily soluble in ether, chloroform, &c. A nitrobenzil melting at 110° has been previously described by Zinin (*Annalen, suppl. Bd.* **3**, 154).

Nitrobenzil-α-dioxime, $C_{14}H_{11}N_3O_4$, separates in colourless crystals when nitrobenzil is warmed for some hours with hydroxylamine hydrochloride (2½ mols.) in alcoholic solution. It melts at 225° with decomposition, and is very sparingly soluble in alcohol, ether, benzene,

&c., but soluble in soda, yielding a deep-yellow solution; it is slowly decomposed by concentrated hydrochloric acid at 100°. The *β-dioxime*, $C_{11}H_{11}N_3O_4$, is formed when an alcoholic solution of the α-compound is heated at 160—170° for several hours. It crystallises from a mixture of benzene and chloroform in colourless needles, melts at 185°, and decomposes at a higher temperature; it is very readily soluble in alcohol, dissolves in soda with a yellow coloration, and is slowly decomposed by concentrated hydrochloric acid.

F. S. K.

Xylalphthalide and its Derivatives. By E. HEILMANN (*Chem. Centr.*, 1890, i, 27—28).—By the action of phthalic anhydride on metatoluylacetic acid, the author has prepared *metaxylalphthalide*; when this is warmed on the water-bath with aqueous potash, it is converted into *metamethyldeoxybenzoïnorthocarboxylic acid*,

$$C_6H_4Me\cdot CH_2\cdot CO\cdot C_6H_4\cdot COOH,$$

which melts at 111—112°. Hydroxylamine reacts with this acid with formation of the *oximidolactone* of *xylylphenylacetoximeorthocarboxylic acid*, $CO<\genfrac{}{}{0pt}{}{C_6H_4}{O\cdot N}>C\cdot CH_2\cdot C_7H_7$, melting at 133—134°.

By protracted heating with alcoholic ammonia under high pressure, the phthalide is converted into *methyldeoxybenzoïncarboxylamide*, $C_6H_4Me\cdot CH_2\cdot CO\cdot C_6H_4\cdot CONH_2$, which melts at 125°. This is a very unstable substance, and loses water very readily, *metaxylalphthalimidine*, $CO<\genfrac{}{}{0pt}{}{C_6H_4}{NH}>C\colon CH\cdot C_7H_7$, being formed, which melts at 165°. By the action of nitrous anhydride in benzene solution, *nitroxylalphthalimidine*, $CO<\genfrac{}{}{0pt}{}{C_6H_4}{NH}>C\colon C(NO_2)\cdot C_7H_7$, is formed, melting at 157—159°.

Nitrous acid reacts with xylalphthalide, producing *xylalphthalnitronitrite*, $CO<\genfrac{}{}{0pt}{}{C_6H_4}{—O}>C(NO_2)\cdot CH(NO_2)\cdot C_7H_7$, from which, by the action of alcohol, nitrous acid is liberated and *nitroxylalphthalide*, $CO<\genfrac{}{}{0pt}{}{C_6H_4}{—O}>C\colon C(NO_2)\cdot C_7H_7$, is formed. It melts at 144° with decomposition, and reacts with potash forming a salt, which when heated is converted into toluylnitromethane. Nitroxylalphthalide is converted on heating into phthalic anhydride and metatoluyl isocyanate.

From nitroxylalphthalide, by reduction with phosphorus and hydrogen iodide, *isoxylalphthalide*, $C_6H_4<\genfrac{}{}{0pt}{}{CH\cdot C\cdot C_7H_7}{CO\cdot O}$, melting at 92—93°, is obtained. Ammonia converts this into *isoxylalphthalimidine*, $C_6H_4<\genfrac{}{}{0pt}{}{CH\colon C\cdot C_7H_7}{CO\cdot NH}$, melting at 196°. Phosphorus oxychloride converts this into 3 : 1-*metatoluylchlorisoquinoline*, melting at 43—45°, which, by treatment with hydrogen iodide and phosphorus, is converted into 3-metatoluylisoquinoline melting at 51—52°.

J. W. L.

Derivatives of 1 : 3-Dichloronaphthalene. By P. T. CLEVE (*Ber.*, **23**, 954—958).—1 : 3-Dichloronaphthalene, obtained from homonucleal dichloro-α-naphthylamine (Abstr., 1887, 494), boils at 289° (291° corr.) under a pressure of 775 mm. The author states that it occurs in so-called α-dichloronaphthalene, together with 1 : 4-dichloronaphthalene, from which it cannot be separated by crystallisation (compare Armstrong and Wynne, Proc., 1888, 106). When its solution in chloroform is saturated with chlorine at the ordinary temperature, and subsequently mixed with alcohol, a trichloronaphthalene, $C_{10}H_5Cl_3$, is obtained, which crystallises from alcohol in white needles, and is regarded as the 1 : 3 : 4-derivative, since it melts at 92°, the melting point of the trichloronaphthalene prepared from 1 : 3 : 4-dichloronaphthol (Abstr., 1888, 597).

Chloronaphthaquinone, $C_{10}H_5ClO_2$, together with phthalic acid, is obtained when 1 : 3-dichloronaphthalene in acetic acid solution is oxidised with chromic acid. It crystallises in long, golden needles, melts at 115°, and is identical with the chloronaphthaquinone obtained by the oxidation of 1 : 3 : 4-dichloronaphthol (Abstr., 1888, 596). The *oxime*, $C_{10}H_5ClO{:}N{\cdot}OH$, crystallises from alcohol in yellowish needles, melts at 200° with decomposition, and is readily soluble in acetic acid and alcohol; the *sodium* salt, $C_{10}H_5ClO{:}N{\cdot}ONa + 2H_2O$, forms small, yellow needles, and is readily soluble in hot water.

Dilute nitric acid (sp. gr. = 1·2) does not seem to act on 1 : 3-dichloronaphthalene at the ordinary temperature. A mixture of concentrated sulphuric and nitric acids, if the latter is not present in too large quantity, converts it into two isomeric dinitrodichloronaphthalenes; with an excess of nitric acid, however, the chief product is a trinitrodichloronaphthalene.

Dinitrodichloronaphthalene I, $C_{10}H_4Cl_2(NO_2)_2$, is the less soluble of the two dinitro-derivatives in acetic acid. It crystallises from acetic acid with 1 mol. prop. of acetic acid in slender, colourless, radially-grouped needles melting at 150°, and from benzene in short, pale-yellow tables, does not dissolve in aqueous soda, and is not oxidised by chromic acid. *Dinitrodichloronaphthalene II* crystallises in small, white needles, melts at 158°, is sparingly soluble in alcohol, insoluble in aqueous soda, and, like the preceding compound, yields the same trinitrodichloronaphthalene on treatment with a mixture of nitric and sulphuric acids. The trinitrodichloronaphthalene crystallises from acetic acid in pale-yellow, compact needles, melts at 178°, dissolves sparingly in alcohol, and is identical with the product obtained by Widman by nitrating so-called α-dichloronaphthalene.

Amidochlorotrinitronaphthalene, $NH_2{\cdot}C_{10}H_3Cl(NO_2)_3$, obtained by heating trinitrodichloronaphthalene with alcoholic ammonia in a water-bath, crystallises with 1 mol. prop. of alcohol in long, slender, lemon-yellow needles, melts at 252°, and is destitute of basic properties.

Anilidochlorotrinitronaphthalene, $NHPh{\cdot}C_{10}H_3Cl(NO_2)_3$, formed by warming a solution of trinitrodichloronaphthalene in aniline, crystallises in red scales, melts at 230°, and is very sparingly soluble in alcohol and acetic acid.

Trinitrochloronaphthol, $OH·C_{10}H_3Cl(NO_2)_3$, prepared by warming trinitrodichloronaphthalene with aqueous soda and some alcohol, crystallises from acetic acid with 1 mol. prop. of acetic acid in pale-yellow needles, melts at 156° with decomposition, and is readily soluble in alcohol and acetic acid. It has strongly acid properties, and forms crystalline, orange-coloured salts with bases. The *barium* salt crystallises with 1 mol. prop. H_2O in brick-red needles, and is very sparingly soluble in hot water; the *calcium* salt forms thin, rectangular tables; the *potassium*, *silver*, and *lead* salts crystallise in needles, and are sparingly soluble in cold water. W. P. W.

ar.-Tetrahydro-β-naphthol. By E. BAMBERGER and M. KITSCHELT (*Ber.*, **23**, 885—887).—The product obtained by reducing β-naphthol with sodium and boiling amyl alcohol consists chiefly of ac.-tetrahydro-β-naphthol (Bamberger and Lodter, this vol., p. 506). The "aromatic" derivative simultaneously formed is contained partly in the amyl alcohol solution, but chiefly in the alkaline liquor employed in the purification of the "alicyclic" compound, and is separated from the latter by first extracting any "alicyclic" compound with ether, then acidifying, and finally steam-distilling the acid liquid. To obtain the small quantity dissolved in the amyl alcohol, the reduction-product is worked up by the method already described (*loc. cit.*), and the alkaline extract of the fractions boiling at 170—186° and 186—196° under a pressure of 55 mm. is freed from any "alicyclic" derivative by steam-distillation; it is then acidified and the ar.-tetrahydro-β-naphthol separated by steam-distillation. The aqueous distillates of the "aromatic" derivative from both sources are united, saturated with salt, extracted with ether, and then fractionated. The yield from 96 grams of β-naphthol amounts to 8 grams of ar.- and 30 grams of ac.-tetrahydro-β-naphthol.

ar.-Tetrahydro-β-naphthol, $C_{10}H_{11}·OH$ (compare this vol., p. 631), crystallises in lustrous, silvery, flat needles, melts at 58°, boils at 275° (therm. in vapour) under a pressure of 707 mm., and is readily soluble in ether, alcohol, benzene, chloroform, and hot light petroleum, sparingly soluble in hot water. Its odour recalls that of creosote. In its reactions it differs from β-naphthol; thus, its aqueous solution gives a white, flocculent precipitate when treated with bleaching powder, a bluish-green coloration with ferric chloride, changing into brownish-yellow flocks on warming, and a greenish-yellow colour on treatment with chloroform and aqueous soda. Its solution in concentrated sulphuric acid gives, on addition of a small quantity of sodium nitrite, a rose-red colour, which changes to a beautiful reddish-violet on warming. ar.-Tetrahydro-β-naphthol exhibits all the reactions of a phenol, and resembles ar.-tetrahydro-α-naphthol in its properties (Bamberger and Althausse, Abstr., 1888, 960; Bamberger and Bordt, this vol., p. 508). The azo-compound, obtained by combination with diazotised sulphanilic acid, is bordeaux-red in colour.

W. P. W.

2 : 2′-Dihydroxynaphthalene. By A. CLAUSIUS (*Ber.*, **23**, 517—529).—2 : 2′-Dihydroxynaphthalene (α-dihydroxynaphthalene of Ebert and Merz, this Journal, 1876, ii, 408) crystallises from water

in long, compact needles, from dilute alcohol in slender, white needles, and from acetic acid in scales, and melts at 190° (not at 186°). Its solution in aqueous alkalis becomes brown on exposure to the air. The acetyl-compound melts at 136° (129° according to Weber, Abstr., 1882, 205), and the benzoyl-compound at 139°.

2′ : 1 : 2-*Hydroxynaphthaquinonoxime*,

$$C_{10}H_6O_2{:}N{\cdot}OH\ [OH : N{\cdot}OH : O = 2' : 1 : 2],$$

is obtained by adding the calculated quantity of sodium nitrite to 2 : 2′-dihydroxynaphthalene suspended in dilute hydrochloric acid. It crystallises from alcohol in small, lustrous, brownish-yellow needles, and melts at about 235°. Contrary to expectation, it was not found possible to introduce a second nitroso-group into the molecule by treating the compound with a further quantity of nitrite. On reduction with the calculated quantity of stannous chloride in hydrochloric acid solution, it yields the *hydrochloride* of the corresponding 2′ : 2 : 1-*dihydroxyamidonaphthalene*, $C_{10}H_5(OH)_2{\cdot}NH_2,HCl$, which crystallises from the solution, on addition of an excess of concentrated hydrochloric acid, in small, lustrous, greyish-white needles or scales, which rapidly become blue on exposure to the air. When oxidised in aqueous solution with an excess of dilute aqueous ferric chloride, the amido-derivative is converted into 2′ : 1 : 2-*hydroxynaphthaquinone*, $C_{10}H_5O_2{\cdot}OH\ [OH : O : O = 2' : 1 : 2]$, which could not be obtained in a crystalline form. It is insoluble in ether, chloroform, and benzene, but readily soluble in alcohol and acetic acid, from which it is precipitated in an amorphous form by the addition of water. Alkalis dissolve it forming reddish-brown solutions, and it seems to interact with sodium sulphite, since it is not precipitated from the aqueous solution of the two compounds on the addition of an acid.

1 : 2 : 2′-*Benzeneazodihydroxynaphthalene*,

$$OH{\cdot}C_{10}H_5O{:}N{\cdot}NHPh\ [N_2HPh : O : OH = 1 : 2 : 2'],$$

is prepared by adding the calculated quantity of diazobenzene chlo ride to an alkaline solution of 2 : 2′-dihydroxynaphthalene. It crystallises in thick, beautiful, greenish-black needles, showing a marked metallic lustre, melts at 220°, and is readily soluble in alkalis, hot alcohol, and benzene. The *acetyl*-derivative, $C_{16}H_{11}ON_2{\cdot}OAc$, crystallises from alcohol in lustrous, steel-blue needles or scales, which appear reddish-yellow by reflected light and melt at 181°. The *ethoxy*-derivative, $C_{16}H_{11}ON_2{\cdot}OEt$, is obtained by dissolving the azo-compound in alcohol, adding the calculated quantity of sodium ethoxide and heating with an excess of ethyl bromide for some time in a reflux apparatus; it crystallises in dark-green, seemingly cubical forms showing a strong metallic lustre, melts at 137°, and is readily soluble in hot alcohol and acetic acid.

1 : 2 : 2′-β-*Naphthaleneazodihydroxynaphthalene*,

$$OH{\cdot}C_{10}H_5O{:}N{\cdot}NHC_{10}H_7,$$

crystallises in greenish needles showing a metallic lustre, and melts at 202°.

1 : 1′ : 2 : 2′-*Dichlorodihydroxynaphthalene*, $C_{10}H_6O_2Cl_2$ [Cl_2 : $(OH)_2$ = 1 : 1′ : 2 : 2′], is formed when chlorine is passed through a cold 10 per cent. solution of 2 : 2′-dihydroxynaphthalene until a considerable separation of colourless needles is obtained. It crystallises from acetic acid in compact needles, melts at 192°, and yields a *diacetyl*-derivative, $C_{10}H_4Cl_2(OAc)_2$, which crystallises in white needles, melts at 195°, and is readily soluble in alcohol and acetic acid.

1 : 3 : 3′ : 1′ : 2 : 2′-*Tetrachlorodihydroxynaphthalene*,

$$C_{10}H_4O_2Cl_4\,[Cl_4 : (OH)_2 = 1 : 3 : 3' : 1' : 2 : 2'],$$

cannot be prepared directly by the action of chlorine on 2 : 2′-dihydroxynaphthalene; it is, however, readily obtained by adding an excess of stannous chloride to a solution of decachloro-2 : 2′-diketohydronaphthalene (*vide infra*). It crystallises from dilute alcohol in long, slender needles, melts at 176°, is readily soluble in alcohol and hot acetic acid, and yields no definite product on oxidation with nitric or chromic acids. The *diacetyl*-derivative, $C_{10}H_2O_2Cl_4(OAc)_2$, crystallises in white needles, melts at 196°, and is readily soluble in alcohol and acetic acid.

Decachloro-2 : 2′-*diketohydronaphthalene*,

$$C_{10}H_2Cl_{10}O_2\,[(Cl_2 : O : Cl_2 : H,Cl)_2 = 1 : 2 : 3 : 4 : 1' : 2' : 3' : 4'],$$

is obtained by passing a slow current of chlorine through a 10 per cent. acetic acid solution of 2 : 2′-dihydroxynaphthalene during 2—3 days. The dichlorodihydroxynaphthalene which at first separates redissolves after some time, and the dark liquid becomes lighter in colour. When completely saturated with chlorine, the liquid is allowed to remain in a closed vessel in the cold for about eight days, then poured off from the crystalline separation, again treated with chlorine and allowed to stand, the process being repeated until no further crystalline separation occurs. It crystallises from a mixture of ether and light petroleum in well-formed, colourless octahedra, melts at 200° with decomposition, and is tolerably sparingly soluble in alcohol, acetic acid, and light petroleum. On treatment with sodium sulphite, it is not reduced, but eliminates hydrogen chloride, forming a compound which melts at 220°, and has all the properties of a pure substance, but, on analysis, gives numbers which do not agree with any probable formula; the same compound is also formed by the action of potassium acetate.

When 2 : 2′-dihydroxynaphthalene is heated with calcium chloride and aniline at 280—290° for 18 hours, a mixture of dianilidonaphthalene with a small proportion of hydroxyanilidonaphthalene is obtained. The latter, together with any unattacked dihydroxynaphthalene, is extracted from the product by treatment with aqueous soda, and the residue purified by crystallisation from alcohol, and finally from benzene. 2 : 2′-*Dianilidonaphthalene*, $C_{10}H_6(NHPh)_2$, crystallises from benzene in colourless, lustrous scales, and melts at 168°. Its *diacetyl*-derivative, $C_{10}H_6(NAcPh)_2$, forms small, pale-yellow crystals, and melts at 197·5°. The *benzeneazo*-derivative, $PhN_2{\cdot}C_{10}H_5(NHPh)_2$, crystallises from alcohol in small, brownish needles. 2 : 2′-*Hydroxyanilidonaphthalene*, $OH{\cdot}C_{10}H_6{\cdot}NHPh$, crystallises in small, pale-

coloured needles, melts at 163°, and is readily soluble in alcohol, benzene, and acetic acid. W. P. W.

β-Nitroso-α-naphthylamine. By A. HARDEN (*Annalen*, **255**, 148—162).—*β-Nitroso-α-naphthylamine*, $C_{10}H_6<\begin{matrix}NH_2\\ | \\ N\end{matrix}>O$, is best prepared by heating a finely-divided mixture of β-nitroso-α-naphthol (10 grams), ammonium chloride (20 grams), and ammonium acetate (50 grams) for 30 minutes on the water-bath, with constant stirring, and keeping the mixture alkaline by the frequent addition of small quantities of ammonium carbonate. The whole is then treated with cold water, the solution filtered, and the residue recrystallised from boiling benzene; the yield is 80 per cent. of the nitrosonaphthol employed. It separates from boiling benzene in small, reddish-brown forms, or in short prisms, with a green reflex, and is readily soluble in hot benzene and alcohol, less readily in ether and chloroform, and only sparingly in light petroleum and hot water. It is insoluble in, and is decomposed by, cold alkalis, but it dissolves freely in acids, and, on boiling, nitrosonaphthol separates from the solution. The *hydrochloride*, $C_{10}H_8N_2O,HCl$, prepared by treating the base with an alcoholic solution of hydrochloric acid and precipitating with ether, crystallises in long, red needles, and is very readily soluble in water and alcohol. The *platinochloride*, $(C_{10}H_8N_2O)_2,H_2PtCl_6$, obtained by adding platinic chloride, and then a large quantity of ether, to a concentrated aqueous solution of the base, is a light-red, amorphous compound, sparingly soluble in cold alcohol and water; it is decomposed by boiling water. The *sulphate*, $C_{10}H_8N_2O,H_2SO_4 + H_2O$, separates as a light-red, crystalline precipitate when ether is added to an alcoholic sulphuric acid solution of the base. The compound $C_{10}H_8N_2O,NaOH$ is precipitated in small, light-brown crystals on adding concentrated soda to an alcoholic solution of the base; it is very hygroscopic.

When β-nitroso-α-naphthylamine is treated with hydroxylamine hydrochloride in cold alcoholic solution, it is converted into orthonaphthylenedioxime (m. p. 149°), identical with the compound described by Goldschmidt and Schmid (Abstr., 1884, 1327); on reduction with ammonium sulphide, it is converted into αβ-naphthylenediamine (Griess, Abstr., 1883, 181). Potassium ferricyanide in alkaline solution oxidises the nitroso-base to orthonaphthylenedioxime anhydride (m. p. 78°).

When an alcoholic solution of nitrosonaphthylamine (2 grams) is mixed with an aqueous solution of potassium nitrite (2 grams), hydrochloric acid (1 mol.) gradually added, and the mixture boiled for five minutes and cooled, a potassium derivative separates in colourless plates. This has probably the constitution $C_{10}H_6<\begin{matrix}N(OH):NO\cdot NO\\ | \\ N\cdot OK\end{matrix}$.
It crystallises from water very slowly in colourless needles containing $1\frac{1}{4}$ mols. H_2O; the anhydrous compound is stable at 180°, but explodes at 250°. In its dilute solutions, barium, iron, and copper salts produce colourless, amorphous precipitates; the *silver*-derivative is amorphous, insoluble in water and alcohol, and stable in the light. When the potassium salt is treated with boiling concentrated hydro-

chloric acid, nitrogen is evolved, and, on cooling, nitrosonaphthol separates from the solution. It is also decomposed by cold dilute sulphuric acid, yielding a colourless, amorphous compound which explodes violently at 111°, and is so unstable that it cannot be obtained in a pure condition; if a solution of the potassium salt is warmed with excess of dilute sulphuric acid, the precipitate first produced gradually dissolves, and the filtered solution, on cooling, deposits a crystalline compound which melts at 212—2.5°, and explodes at a slightly higher temperature. This substance has probably the constitution $C_{10}H_6<\genfrac{}{}{0pt}{}{N(OH)}{\underset{N}{|}}\!\!>\!N$; it crystallises unchanged from boiling hydrochloric acid, dissolves unchanged in concentrated sulphuric acid, and forms salts with alkalis. The *silver* salt, $C_{10}H_6N_3(OH),AgNO_3$, is a colourless, amorphous compound, which explodes at 233°, and is only sparingly soluble in boiling water.

α-Nitroso-β-naphthylamine and β-nitroso-α-naphthylamine both react with phenylhydrazine in the same way, but the products obtained from the β-nitroso-base cannot be obtained in a pure condition.

α-Azoxy-β-naphthylamine, $ON_2 \cdot (C_{10}H_6 \cdot NH_2)_2$, is formed when an alcoholic solution of the α-nitroso-base is kept in the cold for 48 hours with phenylhydrazine and a slight excess of acetic acid. After adding water and shaking for some time, the black, resinous precipitate is separated, spread on a porous plate, and purified by recrystallising from dilute alcohol with addition of animal charcoal. It forms small, red needles, melts at 121—122°, and dissolves freely in concentrated hydrochloric acid, but is reprecipitated on adding water.

α-Phenylorthonaphthylenediamine, $NH_2 \cdot C_{10}H_6 \cdot NHPh$, is prepared by gradually adding phenylhydrazine hydrochloride (3·5 grams) to a boiling alcoholic solution of α-nitroso-β-naphthylamine (4 grams), precipitating the salt thus produced with ether, and decomposing it with sodium carbonate. It crystallises from benzene in small, colourless needles, melts at 161°, and is moderately easily soluble in water.

β-Nitroso-α-ethylnaphthylamine, $C_{10}H_6<\genfrac{}{}{0pt}{}{NHEt}{\underset{N}{|}}\!\!>\!O$, is obtained when β-nitroso-α-naphthol is heated with ethylamine acetate and ethylamine hydrochloride for 20 minutes on the water-bath with frequent addition of ethylamine carbonate; the yield is very small. It crystallises from alcohol in green plates containing 1 mol. H_2O, melts at 95°, and gradually effloresces and turns brown on exposure to the air.

When β-nitroso-α-naphthol is heated with aniline at 100°, β-naphthaquinonedianilide (m. p. 181°) is formed. F. S. K.

ac.- and ar.-Tetrahydro-β-naphthylamine. By E. BAMBERGER and M. KITSCHELT (*Ber.*, 23, 876—884).—It is stated in earlier communications (Abstr., 1888, 599, 712) that the products obtained on reducing β-naphthylamine with sodium and boiling amyl alcohol consist of ac.-tetrahydro-β-naphthylamine and small quantities of dihydronaphthalene and ammonia, a certain proportion of the β-naphthylamine employed escaping reduction. The authors now find that when the proportion of sodium used is raised from 12 to 20 grams for each 15 grams of β-naphthylamine so as to ensure a

practically complete reduction of the base, an increase in the yield of ac.-tetrahydro-β-naphthylamine is not obtained, but in its place a corresponding quantity of ar.-tetrahydro-β-naphthylamine is formed. It is probable that the "aromatic" derivative was formed in small quantity in the earlier experiments, but escaped detection through being mixed with the relatively large quantity of unattacked β-naphthylamine; β-naphthylamine, therefore, behaves like its ethyl-derivative (Bamberger and Müller, Abstr., 1889, 888) in yielding a mixture of "alicyclic" and "aromatic" tetrahydro-bases on reduction.

ac.-Tetrahydro-β-naphthylamine is characterised by yielding a well crystallised acetate and a sparingly soluble nitrate. The *acetate*, $C_{10}H_{11}\cdot NH_2,C_2H_4O_2$, crystallises in thick, lustrous, monoclinic prisms $a : b : c = 1{\cdot}4835 : 1 : 1{\cdot}8018$; $\beta = 78° 24'$, observed faces ∞P, $-P\infty$, $+P\infty$, and $0P$, melts at 155·5—156°, is sparingly soluble in ether, soluble in alcohol, and still more soluble in water, and effloresces on lengthened exposure to the air. The *nitrate*, $C_{10}H_{11}\cdot NH_2,HNO_3$, is precipitated in white scales when nitric acid or potassium nitrate is added to a solution of a soluble salt of the base. It crystallises from water in satiny tables, melts at 210—212°, decomposes when heated at 220° with explosion yielding a distillate containing water, naphthalene, and a quantity of the nitrate, and is sparingly soluble in cold, readily soluble in hot water. *ac.-Benzylidenetetrahydro-β-naphthylamine*, $C_{10}H_{11}\cdot N\colon CHPh$, obtained by heating ac.-tetrahydro-β-naphthylamine carbonate with benzaldehyde at 100°, crystallises in colourless, lustrous, triclinic prisms, melts at 51·5—52°, is readily soluble in light petroleum, ether, benzene, and hot alcohol, insoluble in water, and is very readily decomposed into its generators on treatment with acids. On oxidation with potassium permanganate, ac.-tetrahydro-β-naphthylamine is known to yield a mixture of hydrocinnamorthocarboxylic acid and phthalic acid. When oxidised with a mixture of potassium dichromate and dilute sulphuric acid, the pure base gives, in addition to phthalic acid, a small yield of α-naphthol and α-naphthaquinone; and since experiment shows that α-naphthol yields but the merest trace of α-naphthaquinone under like conditions, it is evident that these two substances are independent oxidation-products. The formation of these α-derivatives from ac.-tetrahydro-β-naphthylamine is due in all probability to the oxidation of dihydronaphthalene, into which the base decomposes under certain conditions (Abstr., 1888, 712). Oxidation with boiling dilute nitric acid (1 gram of 75 per cent. acid to 7 grams of water) converts the base into a mixture of phthalic acid, naphthalene, and several other compounds which have not been further examined.

ar.-Tetrahydro-β-naphthylamine, $C_{10}H_{11}\cdot NH_2$, occurs to the extent of 3—4 per cent. in the product obtained by the reduction of β-naphthylamine. To separate it, the mixed hydrochlorides (compare Abstr., 1888, 599) are dissolved in water, and the solution rendered alkaline by the careful addition of aqueous soda, is steam-distilled. The distillate, after acidification, is concentrated, then rendered alkaline, and extracted with ether; the ether is removed by evaporation, the residue dissolved in light petroleum, and the base further purified by passing a current of moist carbonic anhydride through the solution

in order to convert any trace of the "alicyclic" derivative into its sparingly soluble carbonate, and finally fractionated. It crystallises from light petroleum in lustrous, silvery, flat needles, has an odour recalling that of aniline, melts at 38°, boils at 275—277° (therm. in vapour) under a pressure of 713 mm., and dissolves without difficulty in the ordinary organic solvents. In its reactions it resembles ar.-tetrahydro-α-naphthylamine (Bamberger and Althausse, Abstr., 1888, 959; Bamberger and Bordt, Abstr., 1889, 715); thus, it is neutral in reaction, forms acid salts with mineral acids, can be diazotised in the usual way, reacts with diazo-compounds forming azo-dyes, &c. On oxidation with potassium permanganate, it yields adipic acid. When its diazo-compound is boiled with dilute sulphuric acid, it is converted into *ar.-tetrahydro-β-naphthol*, $C_{10}H_{11}\cdot OH$, which crystallises in silvery, flat needles, melts at 58°, boils at 275°, and is identical with the "aromatic" derivative obtained by reducing β-naphthol in the usual way (see p. 627). W. P. W.

Aromatic Carbamide Chlorides. By O. Kym (*Ber.*, **23**, 424—431).—When carbonyl chloride, dissolved in toluene, is added to a benzene solution of phenyl-β-naphthylcarbamide, no alteration takes place in the cold for an hour; subsequently, separation of phenyl-β-naphthylcarbamide hydrochloride takes place slowly. The reaction proceeds rapidly at 100°, according to the equation $2NHPh\cdot C_{10}H_7 + COCl_2 = C_{10}H_7\cdot NPH\cdot COCl + NHPh\cdot C_{10}H_7,HCl$. The hydrochloride is filtered off, the filtrate concentrated, and the greyish, nodular crystals which separate washed with dilute alcohol, and repeatedly crystallised from hot alcohol. These consist of *phenyl-β-naphthylcarbamide chloride*, and form small, lustrous, white plates, melting at 101—102°, and sparingly soluble in cold alcohol and acetic acid, readily in the hot liquids and in benzene.

Asymmetrical phenyl-β-naphthylcarbamide, $C_{10}H_7\cdot NPh\cdot CO\cdot NH_2$. is prepared by acting on the foregoing compound with alcoholic ammonia at 120°. It crystallises in long, white needles melting at 189—190°, and is very slightly soluble in cold alcohol, benzene, and acetic acid, more readily in the hot liquids.

Diphenyl-β-naphthyl carbamide, $CO(NPh\cdot C_{10}H_7)_2$, is obtained by heating a solution of phenyl-β-naphthylcarbamide chloride in chloroform with aniline (2 mols.). It forms small, white plates melting at 132—133°. It is readily soluble in benzene, less so in acetic acid, and still less in alcohol.

If diphenyl-β-naphthylcarbamide be heated with excess of aniline, it is converted into diphenylcarbamide and phenyl-β-naphthylamine, a reaction similar to that observed by Michler in the case of triphenylcarbamide (this Journal, 1876, ii, 91). Phenyl-β-naphthylamine is also obtained by boiling the above chloride with alcoholic potash.

β-Dinaphthylcarbamide chloride, $N(C_{10}H_7)_2\cdot COCl$.—Carbonyl chloride only acts on β-dinaphthylamine in benzene solution at a temperature of 130—160° (compare next abstract), the reaction then proceeding just as with phenyl-β-naphthylamine. The β-dinaphthylamine hydrochloride is filtered off, the filtrate evaporated, and hydrogen chloride passed in to remove the last portions of β-dinaphthylamine,

the liquid again filtered, and alcohol added to the filtrate. The yellowish substance which separates on cooling is purified by redissolving it in hot benzene and adding alcohol. β-Dinaphthylcarbamide chloride forms white, cauliflower-like aggregates, which melt at 173°, and are very soluble in benzene, readily in hot acetic acid, but almost insoluble in alcohol.

Asymmetrical-β-naphthylcarbamide, $N(C_{10}H_7)_2 \cdot CO \cdot NH_2$, is prepared by acting on the chloride with alcoholic ammonia at 120°. It crystallises in fascicular groups of slender needles which melt at 192—193°, and are sparingly soluble in cold alcohol, acetic acid, and benzene, more readily in the hot liquids.

Phenyl-β-dinaphthylcarbamide, $N(C_{10}H_7)_2 \cdot CO \cdot NHPh$, is prepared by heating aniline and a chloroform solution of β-dinaphthylcarbamide at 130°. It forms fascicular aggregates of long, white needles which melt at 181—182°, and are probably identical with the compound obtained by Gebhardt (Abstr., 1885, 384). By heating with excess of aniline, it is decomposed into β-dinaphthylamine and diphenylcarbamide. β-Dinaphthylcarbamide chloride is also decomposed by alcoholic potash, with formation of β-dinaphthylamine.

Attempts were also made to obtain β-tetranaphthylcarbamide by acting on the chloride with β-dinaphthylamine, but without success (compare next abstract). H. G. C.

β-Dinaphthylcarbamide Chloride. By B. Kühn and N. Landau (*Ber.*, **23**, 811—812).—Contrary to the statement of Kym, in the foregoing abstract, the authors find that carbonyl chloride and β-dinaphthylamine react readily at the ordinary temperature, forming β-dinaphthylamine hydrochloride and β-dinaphthylcarbamide chloride. The latter was crystallised from acetic acid and melted at 172—173° (uncorr.). They also find that β-tetranaphthylcarbamide may be readily obtained by mixing β-dinaphthylamine with β-dinaphthylcarbamide chloride in molecular proportion, and heating them to 190—200°, a little zinc-dust being added to the melt. This is then dissolved in benzene, hydrogen chloride passed into the solution, the filtrate evaporated, and the residue crystallised from acetic acid. β-Tetranaphthylcarbamide forms yellowish-brown, prismatic needles, melts at 167—169°, and is sparingly soluble in alcohol and ether, readily in benzene and acetic acid.

Phenyl-β-dinaphthylcarbamide may be obtained, in addition to Kym's method, by digesting a solution of β-dinaphthylcarbamide chloride and aniline in alcohol at the ordinary pressure. The authors found the melting point to be 180° (uncorr.).

β-Dinaphthylcarbamide chloride reacts further with nitroamines, phenoxides, and nitrophenoxides; the authors reserve the further investigation of the products. H. G. C.

1 : 4-Nitronaphthalenesulphonic Acid. By P. T. Cleve (*Ber.*, **23**, 958—961).—In addition to the 1 : 4′ and 1 : 1′-nitronaphthalenesulphonic acids, the author finds that the 1 : 4-modification is also formed when naphthalene-α-sulphonic acid is nitrated. To prepare the acid, 1 kilo. of sodium naphthalene-α-sulphonate is gradually added

to a mixture of 750 grams of nitric acid (sp. gr. = 1·4) and 500 grams of nitric acid (sp. gr. = 1·5), and the product subsequently diluted with water, neutralised with chalk, and filtered hot. The filtrate, on cooling, deposits abundance of the calcium salt of the 1 : 4′-acid, this is filtered off, the mother liquor concentrated, and a further separation of calcium salt obtained. This is decomposed with sulphuric acid and the solution evaporated to the crystallising point in order to separate a further quantity of the 1 : 4′-acid; the mother liquor is then neutralised with potassium carbonate, the solution concentrated, and the successive fractions of the potassium salt treated with phosphorus pentachloride. The first fractions give almost pure 1 : 4′-nitronaphthalenesulphonic chloride, the later fractions yield mixtures from which the chloride of the 1 : 4-acid can be obtained by crystallisation from benzene and light petroleum. The mother liquor of the calcium salt contains the 1 : 1′-nitronaphthalenesulphonic acid.

1 : 4-*Nitronaphthalenesulphonic acid*, $NO_2 \cdot C_{10}H_6 \cdot SO_3H$, is obtained by boiling the chloride with baryta-water, and carefully neutralising the solution of the resulting barium salt with sulphuric acid. It forms a very soluble, yellowish, crystalline mass. The *potassium* salt crystallises in thin, silvery needles, and is sparingly soluble in cold water; the *sodium* salt crystallises, with 1 mol. H_2O, in very soluble, thin needles; the *silver* salt crystallises in tolerably soluble, small, yellow needles; the *calcium* salt crystallises, with 2 mols. H_2O, in silvery scales, and dissolves in 37 parts of water at 17° and in 16 parts at 100°; the *barium* salt crystallises, with 1 mol. H_2O, in small needles, and dissolves in 66 parts of cold and 33 parts of boiling water; the *lead* salt crystallises, with 6 mols. H_2O, in very soluble, granular aggregates. The *ethyl* salt, $NO_2 \cdot C_{10}H_6 \cdot SO_3Et$, crystallises from alcohol in large prisms and melts at 93°; the *methyl* salt, $NO_2 \cdot C_{10}H_6 \cdot SO_3Me$, crystallises in small needles, melts at 117°, and is sparingly soluble in alcohol. The *chloride*, $NO_2 \cdot C_{10}H_6 \cdot SO_2Cl$, crystallises from chloroform or benzene in large, yellowish prisms, and melts at 99°; the *amide*, $NO_2 \cdot C_{10}H_6 \cdot SO_2NH_2$, is dimorphous and crystallises in small octahedra or scales melting at 188°. The *bisulphide*, $S_2(C_{10}H_6 \cdot NO_2)_2$, obtained by boiling a solution of the chloride in acetic acid with hydriodic acid, forms greenish-yellow, very sparingly soluble scales, and melts at 186°.

1 : 4-Nitronaphthalenesulphonic acid yields naphthionic acid on reduction with ammonium sulphide; and 1 : 4-nitronaphthalenesulphonamide, when boiled with acetic acid, hydriodic acid, and phosphorus, and afterwards precipitated by ammonia, is converted into the *amide* of naphthionic acid, $NH_2 \cdot C_{10}H_6 \cdot SO_2NH_2$. This crystallises from alcohol in brownish-yellow needles, melts at 206°, and yields a *hydrochloride*, $NH_2 \cdot C_{10}H_6 \cdot SO_2NH_2,HCl$, which crystallises in small, colourless, very sparingly soluble needles, and an *acetyl*-derivative, $NHAc \cdot C_{10}H_6 \cdot SO_2NH_2$, which crystallises from alcohol in small, colourless needles, and melts at 241°. W. P. W.

1 : 1′-Chloronaphthalenesulphonic Acid. By P. T. Cleve (*Ber.*, **23**, 962—963).—When potassium 1 : 1′-nitronaphthalenesulphonate is mixed with phosphorus pentachloride, a very vigorous

reaction takes place, and the whole mass becomes carbonised. If the conditions are modified by suspending the potassium salt in carbon bisulphide and then adding the pentachloride, the reaction proceeds quietly with the evolution of nitrous fumes, and 1 : 1′-chloronaphthalenesulphonic chloride is formed. After spontaneous evaporation of the carbon bisulphide, the product is extracted with water, and the insoluble chloride crystallised from benzene, chloroform, and acetic acid. The chloride is only slowly hydrolysed by heating with water at 150°, and is for the most part decomposed with the formation of sulphuric acid. *Barium* 1 : 1′-*chloronaphthalenesulphonate*, obtained by boiling the chloride with baryta-water, crystallises, with 2 mols. H_2O, in nacreous scales and is tolerably soluble in water; the *potassium* salt forms readily soluble, colourless prisms; the *silver* salt forms readily soluble, colourless, lustrous prisms. The *ethyl* salt, $C_{10}H_6Cl\cdot SO_3Et$, crystallises from alcohol in six-sided, colourless, monoclinic tables, $a : b : c = 1·177 : 1 : 1·323$; $\beta = 80° 57′$, and melts at 67·5°; the *methyl* salt, $C_{10}H_6Cl\cdot SO_3Me$, crystallises from alcohol in colourless, sparingly soluble needles, and melts at 70°. The *chloride*, $C_{10}H_6Cl\cdot SO_2Cl$, forms colourless, thin scales, melts at 101°, and is readily soluble in benzene, alcohol, and acetic acid; the *amide*, $C_{10}H_6Cl\cdot SO_2NH_2$, crystallises in fairly large, lustrous prisms, melts at 196—197°, and is sparingly soluble in alcohol. The *bisulphide*, $S_2(C_{10}H_6Cl)_2$, crystallises from alcohol in tables and melts at 110°.

W. P. W.

α-Hydroxysulphonaphthoic Acid. By K. König (*Ber.*, **23**, 806—810).—α-Hydroxysulphonaphthoic acid (Abstr., 1889, 719) readily decomposes with the elimination of both the COOH- and SO_3H-groups; thus, α-naphthol is formed in considerable quantity when the acid is either boiled with dilute sulphuric acid or heated with water in a sealed tube. The salts of the acid are more stable; the dry sodium salt, when heated at 180°, yields, for example, the sodium salt of the corresponding α-naphtholsulphonic acid.

When warmed with an excess of dilute sulphuric acid, α-hydroxysulphonaphthoic acid is very readily converted into dinitro-α-naphthol (Martius yellow) with the evolution of carbonic anhydride. An intermediate nitration-product, nitro-α-hydroxynaphthoic acid (Schmitt and Burkard, Abstr., 1888, 59) can be obtained by suspending α-hydroxysulphonaphthoic acid in five times its weight of acetic acid and gradually adding the calculated quantity of nitric acid (sp. gr. = 1·48) diluted with four times its volume of acetic acid, and allowing the mixture to remain in the cold until dissolution is complete: the product is then treated with ice-cold water. The nitro-α-hydroxynaphthoic acid so prepared yields paranitronaphthol when heated with water at 150°, and hence contains the nitro-group in the para- and not in the meta-position relatively to the hydroxyl, as stated by Schmitt and Burkard. Comparison shows that α-hydroxynaphthoic acid is much less readily nitrated than α-hydroxysulphonaphthoic acid, whence the author concludes that the SO_3H-group in the latter is in the para-position with respect to the hydroxyl.

Contrary to expectation, α-hydroxysulphonaphthoic acid readily

reacts with diazo-compounds, yielding azo-colours (compare Dahl and Co., Germ. Pat., 51715). This is due, however, to the ready elimination of the COOH-group by the azo-group; the azo-dye obtained by treating the acid with a solution of diazobenzene chloride being identical with benzeneazo-α-naphtholsulphonic acid obtained from Neville and Winther's 1 : 4-naphtholsulphonic acid. It follows, therefore, that α-hydroxysulphonaphthoic acid has the constitution [OH : COOH : SO_3H = 1 : 2 : 4]. W. P. W.

Hydrides of Anthracene and Phenanthrene. By L. Lucas (*Chem. Centr.*, 1890, i, 39).—In the preparation of hexahydroanthracene, Graebe and Liebermann obtained an oily substance, which they did not more closely examine; the author has made this the subject of investigation. When heated with amorphous phosphorus and hydriodic acid (boiling point 127°) at 250°, anthracene is primarily converted into a substance which melts at 87—88°, and which, if subjected to a further digestion, is split up into two substances, a solid and a liquid. The former is *anthracene perhydride*, $C_{14}H_{24}$, melting at 89° and boiling at 277·5°; it sublimes at 100°, and is volatile in steam.

If water is added in the above reaction, *anthracene octohydride*, $C_{14}H_{18}$, and an oily substance are formed. The octohydride melts at 60°, and boils at 295°.

The oily product of both these reactions is the same, *anthracene decahydride*. Its sp. gr. at 20° = 0·9884 (water at 4° = 1); boiling point, 280°. If still more water is used in the reaction, anthracene dihydride is the only product.

When distilled over red-hot pumice, these hydrides are converted into anthracene; at a somewhat lower temperature they remain for the greater part unchanged. If distilled over red-hot zinc-dust, the conversion into anthracene is still more complete. Bromine compounds were not obtained. With fuming nitric acid, the perhydride does not react; when treated with concentrated sulphuric acid and fuming nitric acid, the decahydride, as also the octohydride, forms a yellow precipitate, difficult to manipulate. With concentrated sulphuric acid, the octohydride alone forms a well characterised sulphonic acid; its barium salt has the formula $(C_{14}H_{17}SO_3)_2Ba + H_2O$. With oxidising agents, the perhydride is oxidised to no very well characterised substances; the decahydride is oxidised by chromic mixture to anthraquinone, in addition to which another substance is formed, which was not more fully examined; potassium permanganate oxidises the decahydride to phthalic acid. The octohydride in glacial acetic acid is oxidised by chromic acid to anthraquinone.

Phenanthrene also forms a perhydride, $C_{14}H_{24}$, when heated with amorphous phosphorus and hydriodic acid. Its sp. gr. at 20·5° = 0·9312 (water at 4° = 1); it boils at 268—275°, and melts at about 3°. It is oxidised by chromic acid in glacial acetic acid, the products being indefinite. The same perhydride is obtained from phenanthraquinone, when this is reduced with phosphorus and hydriodic acid. Phenanthrene perhydride is converted into anthracene by distilling over zinc-dust. J. W. L.

Derivatives of Dianthryl. By H. SACHSE (*Chem. Centr.*, 1890, i. 38).—By treating dianthryl dissolved in chloroform with chlorine, *dichlorodianthryl octochloride*, $C_{28}H_{16}Cl_{10}$, is formed, which readily decomposes with separation of hydrogen chloride. When treated with alcoholic potassium hydroxide, the solution of the chloride becomes blood-coloured, and on heating it is converted into the green hexachlorodianthryl, $C_{28}H_{12}Cl_6$. Bromine forms corresponding compounds; the *dibromodianthryl octobromide*, $C_{28}H_{16}Br_{10}$, is somewhat more stable than the chloride, and by the action of alcoholic potash is converted into the *hexabromodianthryl*, $C_{28}H_{12}Br_6$.

Dichlorodianthryl, $C_{28}H_{16}Cl_2$, is prepared from dinitrodianthryl by heating with fuming hydrochloric acid at 180°. Bromine causes the formation of *dibromodianthryl.*

Dianthryl tetrahydride, $C_{28}H_{22}$, is prepared by acting on dianthryl with sodium amalgam; it melts at 248—249°. By bromine it is converted into dibromanthracene. With concentrated sulphuric acid, dianthryl forms a trisulphonic acid. J. W. L.

Massoy Bark Oil. By E. F. R. WOY (*Arch. Pharm.* [3], **28**, 22—48).—This oil is obtained from a plant of the Lauraceæ growing in New Guinea. The crude oil is rather fluid, perfectly clear, and yellow, with an odour resembling that of cloves, and a sharp, burning taste. Its sp. gr. at 10° is 1·0514. Its reaction to litmus is very faintly acid, due to a trace of acetic acid; it contains somewhat over ½ per cent of water, but is free from sulphur and nitrogen. A detailed investigation shows the constituents of the oil to be a new terpene, safrole, eugenol, and small quantities of a creosote-like substance. The new terpene, *massoyene*, $C_{10}H_{16}$, boils at 172°, has a sp. gr. = 0·8619 at 13°, and is dextro-rotatory; it does not agree in character with any terpene hitherto described.

From *safrole* the following four new brominated compounds were obtained:—$CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2Br$, a liquid boiling at 215° under a pressure of 22 mm.; $CH_2{:}O_2{:}C_6H_2Br{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2Br$, fibrous crystals melting at 54°; $CH_2{:}O_2{:}C_6H_2Br{\cdot}CH_2{\cdot}CH{:}CH_2$, a liquid boiling at 185° to 190° under a pressure of 18 mm.;

$$CH_2{:}O_2{:}C_6H_3{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2Br,$$

in small tabular crystals melting at 87°. Further, the pentabromide obtained, although identical with the products described by Schiff, Grimaux, and Knotte, must have the formula

$$CH_2{:}O_2{:}C_6HBr_2{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2Br.$$

Dibromobenzoyleugenol. $CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}C_6H_3(OMe){\cdot}OBz$, crystallises in lustrous plates and melts at 97°; *eugenol ethyl ether tribromide*, isomeric with that described by Wassermann, forms tufts of slender, silky needles, and melts at 92°. J. T.

Hydroxycamphocarboxylic Acid from Camphocarboxylic Acid. By A. HALLER and MINGUIN (*Compt. rend.*, **110**, 410—412).—Ethyl camphocarboxylate, when heated in sealed tubes at 150° to 200° with a small quantity of sodium dissolved in excess of ethyl alcohol,

yields ethyl hydroxycamphocarboxylate, $COOEt{\cdot}C_8H_{14}{\cdot}CH_2{\cdot}COOEt$, identical with the product obtained by the direct etherification of hydroxycamphocarboxylic acid, or by treating the mononitrile, $COOEt{\cdot}C_8H_{14}{\cdot}CH_2{\cdot}CN$, with a solution of hydrogen chloride in alcohol. When treated with excess of aqueous potash, it yields hydroxycamphocarboxylic acid, melting at 228—230° and identical with the acid obtained under other conditions.

It has previously been shown that camphocarboxylic nitrile combines readily with alcohols when heated at 100° with the sodium alkyl oxides. Under these conditions, the closed chain is broken and ethereal salts of hydroxycamphocarboxylic nitrile are formed. The reaction with ethyl camphocarboxylate is similar. It is noteworthy that the presence of cyanogen makes the rupture of the nucleus in $OC<\begin{matrix}CH{\cdot}CN\\ |\\ C_8H_{14}\end{matrix}$ much easier than in $OC<\begin{matrix}CH{\cdot}COOEt\\ |\\ C_8H_{14}\end{matrix}$. C. H. B.

Aloïn from Barbados, Curaçao, and Natal Aloes. By E. GROENEWOLD (*Arch. Pharm.* [3], **28**, 115—139).—I. *Aloïn from Barbados aloes.*—This was obtained as small, pale-yellow, needle-shaped crystals, slightly soluble in cold water, easily soluble in hot water. In boiling water it rapidly becomes brown. It is more soluble in alcohol than in water, and the solution is more stable. Aloïn is only slightly soluble in ether, chloroform, light petroleum, and benzene. Acetic acid dissolves it readily, and this solution is unaffected by the air. The moist crystals very readily become discoloured, especially when exposed to light. The substance melts at 147°. The results of numerous analyses are best expressed by the formula $C_{23}H_{24}O_{10}$, but the author prefers to adopt $C_{16}H_{16}O_7$, which best accords with the bromine- and acetyl-derivatives. If the latter be accepted, then the air-dried crystals obtained from a concentrated alcoholic solution would be expressed by $C_{16}H_{16}O_7 + 3H_2O$ or $3\frac{1}{2}H_2O$. A bromaloïn, $C_{16}H_{13}Br_3O_7 + 4H_2O$, was obtained by pouring an aqueous solution of aloïn into bromine-water, or by pouring bromine-water into the aloïn solution. The two bromo-compounds agreed, excepting a difference of about 1 per cent. in the water of crystallisation. This variation has also been noticed by E. Schmidt.

Acetyl-derivatives were only obtained with difficulty by the action of acetic anhydride on adding either concentrated sulphuric acid drop by drop, or on adding a drop or two of acetic chloride. In the former case, the product occurred sometimes as white, hard, columnar crystals, $C_{16}H_{10}Ac_6O_7$, and sometimes as beautiful, soft, yellow needles, $C_{16}H_{13}Ac_3O_7 + \frac{1}{2}H_2O$. In the latter case, only the yellow needles were obtained.

II. *Aloïn from Curaçao aloes.*—This appears to be identical with that from Barbados aloes.

III. *Aloïn from Natal aloes*, $C_{24}H_{26}O_{10}$ + Aq (various).—This differs both chemically and physically from the two aloïns just considered. It can readily be obtained in the form of large, well-formed crystals; this, together with its resistance to the action of alkalis, distinguishes it from Barbados aloïn. Halogen substitution-products are not readily obtained. Oxidation with nitric acid yields both

oxalic and picric acids. Heated in a capillary tube, the aloïn softens at 180° and melts with decomposition at 210°. The acetyl-derivative appears to be $C_{24}H_{21}Ac_5O_{10}$. Natal aloïn differs from Barbados aloïn in containing a methoxyl-group, as determined both in aloïn, $C_{23}H_{23}(OMe)O_9$, and in acetylaloïn, $C_{23}H_{18}(OMe)Ac_5O_9$. J. T.

Derivatives of Cantharidin. By F. ANDERLINI (*Ber.*, **23**, 485—486; compare Homolka, Abstr., 1886, 723).—Cantharidin is oxidised by prolonged boiling with concentrated nitric acid, but the products cannot be separated from unchanged cantharidin.

Cantharidin phenylhydrazone, $C_{16}H_{18}N_2O_3$, is obtained, together with a compound melting at 130—131°, when cantharidin (1 part) is heated at 135—140° with phenylhydrazine (4 parts) and 50 per cent. acetic acid (2 parts); the two products are separated by crystallisation from benzene. The hydrazone separates from acetone, in which it is readily soluble, in large, rhombic crystals melting at 237—238°; it is insoluble in water, and only sparingly soluble in alcohol and benzene.

The compound melting at 130—131° (see above) has the composition $C_{16}H_{21}N_4O_2$; it separates from benzene and dilute alcohol in colourless crystals, and is readily soluble in boiling water.

A compound of the composition $C_{10}H_{13}NO_3$ is formed when cantharadin is heated at 180° for seven to eight hours with a saturated alcoholic solution of ammonia; it crystallises in small prisms, melts at 200—201°, and is readily soluble in hot water and alcohol, but only sparingly in the cold solvents. F. S. K.

Colouring Matter from Diaptomus analogous to Carrotene. By R. BLANCHARD (*Compt. rend.*, **110**, 292—294).—*Diaptomus bacillifer* was treated with alcohol, and after two months the alcohol, which was only slightly coloured, was decanted off, the organisms triturated with sand, again washed with alcohol, and dried in a vacuum. The bright-red powder thus obtained becomes yellow and finally white when exposed to air even in the dark. The pigment is insoluble in water, ammonia, methyl alcohol, and dilute potash, and only very slightly soluble in hot ethyl alcohol. It dissolves in ether with formation of a red solution, in light petroleum and benzene yielding an orange-brown solution, in chloroform (a rose-red solution), and in carbon bisulphide (a ponceau-red solution). Acids, alkalis, and reducing agents are without action on these solutions.

In order to remove fat, &c., the dried pigment was treated with light petroleum and again dried. The alcohol and the petroleum dissolve some of the pigment and all the fatty and other soluble substances. The residue is exhausted with carbon bisulphide, and the latter, when distilled, leaves a deep carmine-red, oily substance, which, if redissolved in carbon bisulphide and evaporated in a vacuum, solidifies but does not crystallise.

The pigment from *Diaptomus* in some respects resembles the lipochromes, but differs from them in its very slight solubility in alcohol and in the character of its absorption spectrum. Concentrated solutions absorb all rays but the red, and when the solution is diluted the less refrangible rays are transmitted to a greater and

greater extent, but no absorption bands are observed. This pigment, in fact, very closely resembles carrotene, and if not identical with it, at any rate belongs to the same group. It is similar in colour, dissolves in the same solvents, behaves similarly with reagents, and shows a similar absorption spectrum. It dissolves, for example, in strong sulphuric acid, forming a deep indigo-blue liquid, and when the solution is poured into water the colour disappears immediately, but no precipitate is formed. Probably there are several carrotenes, just as there are several chlorophylls and hæmoglobins. It follows from these observations (1) that carrotene is common to both animals and plants; (2) that an animal organism is capable of forming a hydrocarbon. *Diaptomus* also furnishes another example of the occurrence of carrotene in the absence of chlorophyll, as in the carrot, tomato, and pumpkin. C. H. B.

Carrotene and the Green Colouring Matter of Chlorophyll Grains. By H. IMMENDORFF (*Chem. Centr.*, 1890, i, 163—164; *Landw. Jahrb.*, **18**, 507—520).—The author recommends the following method for the separation of carrotene. 500 grams of the leaves are boiled with dilute aqueous soda, the brown-coloured extract poured off, the leaves then washed with water, and pressed as free from the latter as possible. The leaves are next digested with 95—98 per cent. alcohol in glass flasks; if, at the end of 24 hours, one of these flasks with its contents is shaken gently in the sunlight, numberless crystals of metallic lustre of pure carrotene separate. After filtering off these, a small quantity of sodium hydroxide is added to the green filtrate, and the alcohol almost entirely distilled off. The residue is then extracted with light petroleum or ether to which a small quantity of alcohol has been added, until no longer coloured. Occasionally this extract deposited a crop of crystals, although, as Husemann has found, this does not always occur. This second colouring matter was not further examined.

Etiolated barley leaves were also examined for carrotene, and it was only found in those leaves which had an orange-colour; in those which were of a pure lemon-yellow colour it could not be detected. By growing plants in a very weak light, leaves which were light-green coloured were obtained in which carrotene was detected.

Carrotene is undoubtedly the yellow colouring matter of chlorophyll grains, and it is also the cause of the autumnal yellow colour of the leaves. J. W. L.

The Colouring Matters of the Cones of Abies excelsa. By L. MACCHIATI (*Chem. Centr.*, 1890, i, 164; from *Naturwiss. Rundschau.*, **4**, 608).—Alcohol abstracts a yellow colouring matter from the perfectly ripe cones, which gives strong general absorption of the violet end of the spectrum as far as F, and a band between C and E. The alcoholic extract is concentrated, and the residue treated successively with alcohol, ether, and chloroform. The remaining portion is completely soluble in water, to which it imparts a beautiful yellowish-red colour. From this solution, beautiful, triclinic crystals may be obtained, which are now insoluble in alcohol. The substance does not contain

nitrogen. If the cones, after extraction with alcohol as above described, are treated with boiling water, the solution is golden-yellow. This colouring matter appears to be amorphous, but not of a tarry nature. J. W. L.

Pyroglutamic Acid. By F. ANDERLINI (*Gazzetta*, **19**, 99—102).—Haitinger (*Monatsh.*, **3**, 228) prepared pyroglutamic acid by heating glutamic acid at 180—190°, and found that pyrroline is formed by the dry distillation of calcium pyroglutamate; the author therefore considers that pyroglutamic acid is a carboxylic derivative of an oxypyrrolidine, $CH_2<\begin{matrix}CH_2\cdot CH\cdot COOH\\ CO\cdot NH\end{matrix}$.

The pure acid forms small, colourless, transparent crystals belonging to the monoclinic system $a : b : c = 0.8239 : 1 : 0.5281$, and exhibiting hemimorphism; it melts at 182—183°. When reduced with sodium and amyl alcohol, a small quantity of an alkaline product with an odour resembling that of pyrollidine is obtained; hydriodic acid and phosphorus yield ammonia and butyric acid in addition. The action of phosphoric chloride, hydrogen chloride, and methyl iodide gave no definite results.

Silver pyroglutamate, $C_5H_6NO_3Ag$, forms white crystals which melt at 176—180°, and are slowly coloured by exposure to light; it is soluble in dilute alcohol and in boiling water, but only very sparingly in cold water. S. B. A. A.

Pyridine- and Pyrroline-derivatives from Anilidopyrotartaric Acid. By A. REISSERT (*Ber.*, **23**, 542—553).—*Phenyldiketomethylanilidobromopyrrolidine hydrobromide*, $C_{17}H_{15}N_2O_2Br,HBr$, separates in crystals when the lactone of phenylketohydroxydimethylanilidotetrahydropyridinecarboxylic acid (1 mol.) (compare Abstr., 1889, 694) is dissolved in chloroform, and bromine (1 mol.) gradually added to the well-cooled solution; the mother liquors contain a dibromo-compound which is described below. It crystallises with 1 mol. of chloroform, which is expelled at 100°; it is readily soluble in alcohol but insoluble in water.

The free *base*, $\begin{matrix}CHBr\cdot CO\\ NPh-CO\end{matrix}>CMe\cdot NHPh$, prepared by decomposing the hydrobromide with boiling water, crystallises from dilute alcohol in small, colourless needles, melts at 141°, and is readily soluble in benzene, chloroform, alcohol, ether, and glacial acetic acid, but insoluble in water and light petroleum. It dissolves in hot concentrated mineral acids and in alkalis. The *nitroso*-compound, $C_{17}H_{14}N_3O_3Br$, crystallises from alcohol in small needles melting at 199·5°.

Phenyldiketomethylanilidodibromopyrrolidine, $C_{17}H_{14}N_2O_2Br_2$, is obtained when the chloroform mother liquors from the monobromo-compound are evaporated. It crystallises from alcohol in shining plates, and melts at 134°.

Dianilidomethylbromacetoacetic acid,

$$NHPh\cdot CHBr\cdot CO\cdot CMe(NHPh)\cdot COOH,$$

is formed when the monobromo-compound described above is dissolved in hot soda and the resulting sodium salt decomposed with a mineral acid. It crystallises from dilute alcohol and glacial acetic acid in small, colourless needles, melts at 157°, and is readily soluble in alcohol, benzene, ether, and glacial acetic acid; it is reconverted into diketomethylanilidobromopyrrolidine when boiled with concentrated acids. The *sodium* salt crystallises in small needles with 3 mols. H_2O. The acid yields a dinitroso-compound.

Phenylanilidobromomethyl-methylanilidopyrazolone,

$$NPh<\begin{matrix} N:C\cdot CHBr\cdot NHPh \\ CO\cdot CMe\cdot NHPh \end{matrix},$$

is obtained by heating the preceding compound with phenylhydrazine at 140—150°; it is a yellow, semi-crystalline substance, begins to decompose at 70°, and melts completely at 80°.

Phenyldiketomethylanilidodichloropyrrolidine, $C_{17}H_{14}N_2O_2Cl_2$, is formed when the lactone of phenylketohydroxydimethylanilidotetrahydropyridinecarboxylic acid is heated with phosphorus oxychloride and phosphorus pentachloride. It crystallises from alcohol and acetic acid in small plates, melts at 138°, and is readily soluble in benzene and ether.

Dianilidomethyldichloracetic acid, $C_{17}H_{16}N_2O_3Cl_2$, is obtained by boiling the preceding compound with soda and decomposing the product with a mineral acid. It separates from a mixture of chloroform and light petroleum in spherical crystals, melts at 151°, and is readily soluble in benzene, ether, chloroform, and glacial acetic acid, but insoluble in water and light petroleum. F. S. K.

Compounds of Pyridine with Mercury Salts. By A. Groos (*Arch. Pharm.* [3], **28**, 73—78).—The compound with mercury iodide, $HgI_2,2C_5NH_5$ (Monari, *Jahrsb.*, 1884, 644), is obtained when dry mercurous iodide is dissolved in warm pyridine; it melts at 97° (uncorrected). From a solution in cold pyridine to which alcohol was added, crystals 2 cm. long and 4 mm. thick were obtained. The mercury bromide compound, $HgBr_2,2C_5NH_5$, is prepared like the foregoing compound; beautiful crystals are obtained from its alcoholic solution which melt at 127·5°. These substances dissociate readily, and tables of their vapour-tensions are given as determined at 14°, 35·5°, 78°, 99—100°, and 137°. The compounds re-form as the temperature goes down. Corresponding compounds with mercurous nitrate and sulphate were obtained. The separation of mercury in these reactions shows that mercurous salts are not formed, or at least if formed are not stable. The compounds can also be formed from mercuric salts. J. T.

Metallo-quinolides and Double Salts of Quinoline. By E. Borsbach (*Ber.*, **23**, 431—440).—Various double salts of quinoline have been described by Hofmann (*Annalen*, **47**), Bromeis (*Annalen*, **52**), Baeyer (*Ber.*, **12**, 2), and especially by Schiff (*Annalen*, **131**), the last of whom introduced the term metallo-quinolides for the compounds obtained by the direct action of quinoline on metallic salts.

The metallo-quinolides were obtained by simply adding quinoline to the metallic salt, the compound separating, as a rule, immediately, but in certain cases only after some time. The double salts may be obtained by dissolving the foregoing compounds in hydrochloric acid, or by adding quinoline hydrochloride to a solution of the metallic salts. All the compounds are stable in the air, and have the characteristic odour of quinoline, which is more intense in the metallo-quinolides; some are decomposed by acids, and others even by water. With few exceptions, quinoline only gives compounds with the halogen compounds of the heavy metals.

The salt $MnCl_2,C_9NH_7,HCl$ is prepared by dissolving manganous chloride in moderately concentrated hydrochloric acid, and adding quinoline. It crystallises from hydrochloric acid in hair-like needles, which have a rose-red colour when dry, and remain unaltered at 250°.

The salt $FeCl_3,C_9NH_7,HCl$ separates as a yellow, crystalline precipitate when concentrated hydrochloric acid is added to a mixture of strong ferric chloride solution and quinoline. It dissolves again on shaking and warming, and then crystallises in small needles, which melt at 150°, and are decomposed by boiling water.

A double salt with ferrous chloride or sulphate could not be obtained.

The salt $CoCl_2,2C_9NH_7$ is formed by adding quinoline to an alcoholic solution of cobalt chloride. It separates as a thick, blue, amorphous precipitate, but is obtained in well-developed triclinic crystals when a dilute alcoholic solution is mixed with a little quinoline, and allowed to evaporate spontaneously. It is decomposed on heating, and also by water and acids.

Copper salts.—The salt $CuCl_2,2C_9NH_7$ is obtained either amorphous or crystalline in exactly the same manner as with the foregoing cobalt salt. In the amorphous state, it has a bluish-grey colour, but when crystalline it is opaque and almost black. It is converted by hot water into a green basic salt, and is also decomposed by acids. The sulphate and nitrate of copper give flocculent precipitates of basic salts with quinoline. The salt $Cu(C_2H_3O_2)_2,C_9NH_7$ separates as an intensely green, crystalline powder on the addition of quinoline to a concentrated neutral solution of cupric acetate. It is readily soluble in alcohol, less in cold water, and is decomposed by boiling water and by acids.

Zinc salts.—The salt $ZnI_2,2C_9NH_7$ is obtained as a white powder when a solution of zinc iodide is precipitated by quinoline. It is slightly soluble in cold and is somewhat decomposed by hot water, and becomes yellow on exposure to light. The compound with zinc bromide has a similar composition, and forms a white, flocculent powder.

Cadmium Salts.—Cadmium chloride gives with quinoline in aqueous or alcoholic solution a thick, white precipitate of the salt $CdCl_2,C_9NH_7$; this is sparingly soluble in water and alcohol, and dissolves in acids forming double salts. The hydrochloric acid double salt has been previously prepared by Williams. The bromide $CdBr_2,C_9NH_7$ is prepared in the same manner, and crystallises from hot alcohol in small white needles, which are decomposed by boiling water and acids. The salt $CdI_2,2C_9NH_7$ differs in composition from the two

foregoing compounds, but is also decomposed by hot water. From its solution in hydrochloric acid, the double salt separates after a long time in green, hair-like needles which have a metallic lustre, and are insoluble in water.

Tin Salts.—By the action of quinoline on an alcoholic solution of stannous chloride, a thick, white, amorphous precipitate is obtained which has not a constant composition. It dissolves in dilute acids, and, after a time, the double salt $SnCl_2,C_9NH_7,HCl$ separates in long, thin needles which melt at 127°. Stannic chloride yields a similar double salt, $SnCl_4,2(C_9NH_7,HCl)$, which crystallises in long, lustrous needles. The compound $SnCl_4,2(C_9NH_7,HCl) + H_2O$, described by Schiff, could not be obtained.

Mercury Salts.—The mercuric bromide compound, $HgBr_2,C_9NH_7$, is obtained in the usual manner, and forms a white, voluminous precipitate melting at 204°, and almost insoluble in water and alcohol. The mercuric iodide compound, HgI_2,C_9NH_7, crystallises in pale yellow, lustrous plates, soluble in warm alcohol and in solutions of potassium iodide and ammonium salts. It melts at 168°, and decomposes above this temperature. Of the true double salts, only that with mercuric chloride, $2C_9NH_7,H_2HgCl_4 + 2H_2O$, could be obtained; this separates in monoclinic crystals from a solution of mercury-chloride-quinoline in hydrochloric acid after a long time, and may also be obtained by adding quinoline hydrochloride to a solution of mercuric chloride. It melts at 91°, and decomposes at a higher temperature.

An aqueous solution of lead nitrate is precipitated by quinoline, but the product is simply a basic lead salt of the probable formula $Pb(NO_3)_2,Pb(OH)_2$. Nickel chloride does not act in the same manner as cobalt chloride, but appears not to form a compound, or in any case only a most unstable one.

From a solution of aluminium chloride, quinoline precipitates aluminium hydroxide, which dissolves in concentrated hydrochloric acid. On further addition of the latter, a white, crystalline substance separates, which has the formula, $AlCl_3 + 6H_2O$. H. G. C.

Compounds of Alloxan with Pyrazole Bases. By G. Pellizzari (*Annalen*, **255**, 230—251; compare Abstr., 1889, 517, and 1888, 142).—The compound previously described as formylphenyldimethylpyrazolone (formylantipyrine), obtained by boiling phenyldimethylpyrazolonetartronylimide with concentrated hydrochloric acid or potash, has, in reality, the molecular formula $C_{24}H_{24}N_4O_4$, and is *di-phenyldimethylpyrazoloneacetic acid.* The *platinochloride*, $(C_{24}H_{24}N_4O_4)_2,H_2PtCl_6$, is a reddish-brown powder. The *sulphate*, $C_{24}H_{24}N_4O_4,H_2SO_4$, crystallises in long, silky needles, and is sparingly soluble in cold water. The *barium* salt, $(C_{24}H_{23}N_4O_4)_2Ba$, forms transparent, very deliquescent crystals.

Di-phenyldimethylpyrazoloneacetic acid dissolves in concentrated nitric acid; on boiling the solution, carbonic anhydride and oxides of nitrogen are evolved, and nitrophenyldimethylpyrazolone (m. p. 273°) is formed. The *tetrabromo*-derivative, $C_{24}H_{24}N_4O_4Br_4$, prepared by treating the acid with bromine in glacial acetic acid solution, crystallises in yellow needles, melts at 149—151° with decomposition, and is

decomposed by water. The *anilide*, $C_{21}H_{23}N_4O_3\cdot NHPh$, crystallises in colourless needles, melts at 237°, and is very readily soluble in alcohol and acids, but only very sparingly in water, benzene, and ether, and insoluble in cold potash.

Methylenedi-phenyldimethylpyrazolone, $CH_2(C_3N_2Me_2Ph)_2$, is formed when di-phenyldimethylpyrazoloneacetic acid is heated at 240—250° until the evolution of carbonic anhydride is at an end; it can also be obtained by boiling phenyldimethylpyrazolone with formaldehyde and concentrated hydrochloric acid. It separates from alcohol in colourless, monoclinic crystals containing 1 mol. H_2O, $a : b : c = 0{\cdot}83328 : 1 : 0{\cdot}80173$, $\beta = 87° 3' 2''$, and loses its water at 130°, the anhydrous substance melting at 179°. It is readily soluble in water, benzene, glacial acetic acid, and mineral acids, but only sparingly in alcohol and ether, and insoluble in alkalis.

Methylenedi-phenylmethylpyrazolone, $CH_2(C_3N_2HMePh)_2$, can be obtained by boiling methylphenylpyrazolone with formaldehyde and concentrated hydrochloric acid, the hydrochloride separating on cooling in slender, silky needles. The free base is a colourless, amorphous powder, readily soluble in alcohol, benzene, and acetic acid; when heated with methyl iodide at 130° in alcoholic solution, it is converted into methylenedi-phenyldimethylpyrazolone (m. p. 179°). F. S. K.

Morphine from Papaver rhœas. By O. HESSE (*Arch. Pharm.* [3], **28**, 7—9).—Some time ago, Dieterich (*Pharm. Zeit. Russ.*, **27**, 269) claimed to have found in the aqueous and alcoholic extracts of the flower leaves of this poppy 0·7 and 0·17 per cent. respectively of morphine. The author has repeated Dieterich's procedure on 300 grams of fresh leaves, but obtained only a few milligrams of glistening crystals, which, however, were not morphine, but appeared to contain some rhœadine. When fresh material is available, the author will pursue the subject. J. T.

Dextrococaïne. By A. EINHORN and A. MARQUARDT (*Ber.*, **23**, 468—474).—According to Einhorn's formula for cocaïne, two asymmetrical carbon-atoms are present in the molecule; if this is correct, similar optical isomerides should exist to those of atropine. Experiments made to convert cocaïne directly into an isomeric base have not been attended with success, but similar experiments with ecgonine, one of its decomposition-products, have given the desired result, for this compound and all its derivatives, including cocaïne itself, are converted into dextro-ecgonine by warming with an aqueous solution of potassium hydroxide on the water-bath.

The best material for the preparation of dextro-ecgonine is the mixture of alkaloïds obtained as a bye-product in the preparation of cocaïne, which must be warmed with the aqueous potash for 18—24 hours. Dextro-ecgonine, $C_9H_{15}NO_3$, crystallises in tables which seem to be hemimorphous, and melts at 254°. On heating with acetic acid saturated with hydrogen chloride, it yields the same anhydroecgonine as is obtained from ordinary ecgonine, whence it would appear that the optical activity is due to the asymmetrical carbon-

atom in the side chain. The *hydrochloride*, $C_9H_{15}NO_3,HCl$, crystallises from alcohol in monoclinic prisms; an aqueous solution containing 4·4 per cent., in a tube 2 dcm. in length, rotated the plane of polarisation 1·6° to the right. The *aurochloride*, $C_9H_{15}NO_3,HAuCl_4$, forms small, yellow plates which melt with decomposition at 220°. Its *methyl ether*, $C_{10}H_{17}NO_3$, obtained by suspending dextro-ecgonine in methyl alcohol, and passing in hydrogen chloride, crystallises from alcohol in prisms melting at 215°.

Dextrococaïne is prepared by heating the foregoing methyl ether with benzoic chloride. It is an oil, which gives a beautifully crystalline *hydrochloride*, $C_{17}H_{21}NO_4,HCl$, melting at 205°, whereas ordinary cocaïne hydrochloride melts at 181·5°. A solution of 1·9 per cent. of this salt in dilute alcohol of the same strength as employed by Antrick (Abstr., 1887, 506), in a tube 2 dcm. in length, rotated the plane of polarisation 1·5° to the right. The physiological properties of dextro-cocaïne are similar to those of cocaïne, but its action takes place more quickly, and is more transient. H. G. C.

Bye-product from the Commercial Synthesis of Cocaïne. By C. Liebermann and F. Giesel (*Ber.*, **23**, 508—512).—The mother liquors from the cocaïne prepared commercially from ecgonine contain a very small quantity of a compound which is probably *methylcocaïne*, $C_{18}H_{23}NO_4$, but which may possibly be an isomeride of cocaïne. This base separates from ether, chloroform, benzene, and light petroleum as an oil; it is also precipitated in an oily condition on the addition of an alkaline carbonate to its solution in acids, but the oil solidifies on keeping, the crystalline compound melting at 46—47°. The *sulphate* crystallises in small plates and is readily soluble in water but only sparingly in alcohol. The *hydrochloride*, $C_{16}H_{23}NO_4,HCl$, is much less readily soluble in cold water than cocaïne hydrochloride, and crystallises from hot alcohol in needles or prisms melting at 209—210°; it produces the same sensation as cocaïne hydrochloride when placed on the tongue. The *nitrate* is precipitated in crystals on adding nitric acid to dilute solutions of the other salts; this reaction serves as a means of distinguishing between, and separating the methyl-derivative from cocaïne. It is moderately easily soluble in pure water and crystallises well from boiling water and alcohol. The *platinochloride*, $(C_{18}H_{23}NO_4)_2,H_2PtCl_6$, crystallises from hot water in yellowish needles; the aurochloride, $C_{18}H_{23}NO_4,HAuCl_4$, crystallises from dilute alcohol in needles and melts at 148°.

Methylcocaïne is decomposed by water, although much more slowly than cocaïne, and it is decomposed by boiling hydriodic acid with liberation of methyl iodide (1 mol.); it is only slowly acted on by concentrated hydrochloric acid, but much more quickly by the boiling dilute acid, yielding methyl alcohol, benzoic acid, and methylecgonine hydrochloride.

Benzoylmethylecgonine hydrochloride, $C_{17}H_{21}NO_4,HCl$, the first product of the decomposition of methylcocaïne with hydrochloric acid, crystallises from hot water in colourless prisms. The *aurochloride* has the composition $C_{17}H_{21}NO_4,HAuCl_4$. The *nitrate* is sparingly soluble.

Methylecgonine, $C_{10}H_{17}NO_3$, prepared by decomposing the hydro-

chloride with silver oxide, crystallises from strong methyl alcohol, melts at 264° with decomposition, and is very readily soluble in water, but insoluble in absolute alcohol, and only very sparingly soluble in methyl alcohol. The *hydrochloride*, $C_{10}H_{17}NO_3,HCl$, crystallises in needles and melts at 236°. The *aurochloride*, $C_{10}H_{17}NO_3,HAuCl_4$, crystallises in lemon-yellow needles melting at 220°.

Methylcocaïne and methylecgonine may possibly be identical with the dextro-rotatory cocaïne and dextro-rotatory ecgonine described by Einhorn and Marquardt (preceding abstract); experiments will be instituted with the object of testing the correctness of this supposition.

F. S. K.

Berberis Alkaloïds. By E. SCHMIDT and W. KERSTEIN (*Arch. Pharm.* [3], **28**, 49—73).—Although hydrastine hydrochloride and sulphate are used in medicine, the pure salts have not been described.

Hydrastine hydrochloride, $C_{21}H_{21}NO_6,HCl$, was prepared by dissolving hydrastine in anhydrous and alcohol-free ether, and leading dry hydrogen chloride over the surface of this solution as long as the salt was precipitated. This precipitate, after drying over sulphuric acid, formed a white, microcrystalline powder, easily soluble in water and chloroform. The corresponding hydrobromide was very similar in appearance; it is very soluble in chloroform, but somewhat less soluble in water than the former salt. The hydriodide forms a yellowish-brown, microcrystalline powder, much less soluble in water than the two previous salts. Hydrastine sulphate, $C_{21}H_{21}NO_6,H_2SO_4$, was prepared by adding to the ethereal hydrastine solution ether which had been shaken up with concentrated sulphuric acid. This is added drop by drop, an excess being avoided, as long as a precipitate falls. This salt readily takes up moisture and forms a gummy mass. It was found to contain 3 per cent. more sulphuric acid than the commercial article. Hydrastine aurochloride, $C_{21}H_{21}NO_6,HAuCl_4$, was also prepared, but found, like that prepared by Wilhelm, to yield too little gold by over 0·5 per cent.

This investigation confirms the view that hydrastine contains one methoxyl-group less than narcotine, thus:—Hydrastine, $C_{21}H_{21}NO_6$; narcotine, $OMe{\cdot}C_{21}H_{20}NO_6$. Narcotine, when oxidised with chromic acid, was found to yield opianic acid, $C_{10}H_{10}O_5$, and cotarnine, $C_{12}H_{13}NO_3$, whilst hydrastine has been shown by Schmidt and Wilhelm to give opianic acid and hydrastinine, $C_{11}H_{11}NO_2$. Narcotine, when oxidised by potassium permanganate in alkaline solution, gives hemipinic acid, $C_{10}H_{10}O_6$. Goldschmiedt has shown (Abstr., 1888, 362) that papaverine yields isohemipinic acid. This led to an investigation of the hemipinic acids obtained from narcotine, hydrastine, and berberine, and these acids were found to be chemically identical. Besides hemipinic acid, narcotine gives cotarnine, but to isolate this the oxidation was made with barium permanganate, and after removing the barium with sulphuric acid and the hemipinic acid with ether, cotarnine platinochloride was directly precipitated. The amount obtained, however, bore no relation to the amount of base employed, so that decomposition of the cotarnine first formed takes place. Wauklyn and Chapman found that the whole of the nitrogen of nar-

cotine is evolved as ammonia by treatment with an alkaline permanganate solution. In the present investigation, Kerstein found only traces of ammonium salts in the hydrochloric acid employed to collect anything volatilised, whilst Schmidt, in a footnote, remarks that narcotine, when boiled with excess of alkaline potassium permanganate, evolves a strong odour of methylamine. Although the decomposition of narcotine is not very sharply defined, the primary reaction is doubtless expressed by the equation $C_{22}H_{23}NO_3 + O_2 = C_{10}H_{10}O_6 + C_{12}H_{13}NO_3$, narcotine giving hemipinic acid and cotarnine. By the distillation of narcotine and hydrastine, respectively, in hydrogen, considerable quantities of meconine and trimethylamine were obtained.

Boiling acetic anhydride does not act on hydrastine. Acetic chloride, however, gives a compound which crystallises from alcohol in beautiful, yellowish-green needles, whose solution exhibits a bluish-green fluorescence. Analysis leads to the formula $C_{21}H_{20}AcNO_6$. This is undergoing further investigation. On boiling hydrastine with iodine in alcoholic solution, the following reaction takes place: $C_{21}H_{21}NO_6 + 6I + H_2O = C_{10}H_{10}O_5 + C_{11}H_{10}NO_2I,I_2 + 3HI$. Roser (Abstr., 1888, 1115) obtained a similar reaction for narcotine, and from the triiodide, by treatment with hydrogen sulphide, he obtained the two compounds, iodotarconine methiodide, $C_{11}H_8INO_3,MeI$, and tarconine methiodide, $C_{11}H_9NO_3,MeI$, whilst Kerstein has only succeeded in isolating hydrastonine iodide, $C_{11}H_{10}NO_2I$. Still it does not appear improbable that iodohydrastonine iodide will be obtained under suitable conditions.

Ethylhydrastine, $C_{21}H_{20}EtNO_6$, was prepared by heating hydrastine ethiodide with water, and decomposing with normal potash, when an oily liquid separated, which solidified to a yellowish-green mass. This compound, when recrystallised from alcohol, formed yellowish-green needles melting at 127°; it is easily soluble in mineral acids, alcohol, ether, and chloroform, but not in water. The double chlorides of this compound and platinum, gold, and mercury, also the compound with picric acid, were obtained as amorphous powders.

Phytosterin, $C_{26}H_{44}O + H_2O$, separates from extract of hydrastis root after long standing as a smeary, resinous deposit, along with other compounds. After crystallising from glacial acetic acid, and then from alcohol, phytosterin is removed from solution, after acidifying with hydrochloric acid, by shaking up with ether; fat is removed by saponifying with alcoholic potash and treatment of the dry soap with chloroform. Repeated crystallisation of the residue gives phytosterin as small, brilliant, colourless plates, melting at 133°.

J. T.

Alkaloïds of the Root of Stylophoron diphyllum. By F. SELLE (*Arch. Pharm.* [3], **28**, 96—109).—The author has exhaustively examined stylophorine, an alkaloïd obtained from the above root, and finds that it is identical with chelidonine, $C_{20}H_{19}NO_5 + H_2O$. Hydrochloric acid under pressure at 150° does not act on this alkaloïd. When heated with aqueous iodine in a glycerol-bath, no methyl iodide was formed, and silver nitrate solution was scarcely rendered turbid. The base therefore contains no methoxyl-group. Chelidonine, although

the principal alkaloïd of the root examined, is not the only one; at least two others have been detected, which will be further investigated when more material is available. J. T.

Taxine, the Alkaloïd of the Yew-tree (Taxus baccata). By A. Hilger and F. Brande (*Ber.*, **23**, 464—468).—The preparation of this alkaloïd was carried out according to the method given by Marmé (*Med. Centr.*, **14**, 97). The ethereal solution was extracted by dilute sulphuric acid, the extract precipitated with ammonia, and the yellow precipitate redissolved in ether; the process being repeated until the precipitate with ammonia was quite white. Taxine cannot be obtained in crystals; it is readily soluble in alcohol and ether, less so in chloroform, scarcely at all in water, and insoluble in benzene. It melts at 82° evolving a characteristic aromatic odour, and gives an intense, purple-violet coloration with concentrated sulphuric acid, whilst Fröhde's reagent colours it reddish-violet. The slightly acid aqueous solution of the alkaloïd gives precipitates with potassium bismuthoiodide, potassium iodide and iodine, sodium phosphomolybdate, gold chloride, platinic chloride, picric acid, and even fixed alkalis and ammonia. It appears to have the composition $C_{37}H_{52}O_{10}N$.

The salts are soluble in water and difficult to obtain crystalline, only the *hydrochloride*, $C_{37}H_{52}O_{10}N,HCl$, having been prepared in a pure state by passing hydrogen chloride into a solution of the alkaloïd in anhydrous ether. The *platinochloride*, $(C_{37}H_{52}O_{10}N)_2,H_2PtCl_6$, forms a yellow, microcrystalline powder.

Taxine ethiodide, $C_{37}H_{52}O_{10}N,EtI$, is prepared by heating a mixture of the two compounds in molecular proportion at 100° under pressure. It is a crystalline product, which may be purified by dissolving in alcohol, and pouring the solution into water. H. G. C.

Diastatic Ferment of Ungerminated Wheat. By C. J. Lintner (*Bied. Centr.*, **19**, 141; compare Abstr., 1888, 497).—Wheat contains a diastatic ferment, which, like malt-diastase, converts starch into maltose; but it differs from malt-diastase in not having the power of dissolving starch paste. Attempts to isolate the ferment failed. N. H. M.

Physiological Chemistry.

Digestibility of Boiled Milk. By R. W. Raudnitz (*Zeit. physiol. Chem.*, **14**, 325—327).—The author corrects and amplifies a reference he had previously made (Abstr., 1889, 1225) to a paper by W. Prausnitz, on the use of milk as a food (*Zeit. Biol.*, **25**), pointing out that the calcium salts found in the fæces on a milk diet have a threefold origin: (1) from the food, (2) from the digestive juices, (3) salts separated by the intestine, in which it takes the place of the kidneys as excreting organ. W. D. H.

Action of Dilute Hydrochloric Acid and of Pepsin with Hydrochloric Acid on the Digestible Albumin of Fodders. By A. STUTZER (*Landw. Versuchs-Stat.*, 1890, 107—133).—In pursuance of former investigations, the author has examined the action mentioned above, care being taken that the conditions in all the experiments were alike. All the substances to be tested were passed through a 1-mm. sieve, and then of that which passed through, those portions passing a 0·5-mm. sieve were rejected: the material was soaked in water for 12—14 hours, the water being saturated with chloroform to prevent fermentation; it was found that this antiseptic had no influence on the digestion experiments, to which the fodder was submitted. For every 100 milligrams of nitrogen as digestible albumin, the same quantity of liquid was employed, but the composition of the liquid varied with the different experiments, whilst the temperature was "blood-heat." Hydrochloric acid (0·05—0·10 per cent.), with or without pepsin, dissolved notable quantities of albumin, and it was found advisable to use very dilute solutions, but in large quantities. In the case of bran, about one-third of the albumin soluble in pepsin was also soluble in water; dilute hydrochloric acid showed the greatest activity at a temperature of 40° for 60 min., the strength of solution being 0·03 per cent. of hydrogen chloride. Pepsin and hydrochloric acid together (0·03 per cent. hydrogen chloride) was less active than the acid alone, but if more than 0·03 per cent. of the latter was present, then the mixture became more active than the acid alone.

In the case of wheaten bread, 1·651 per cent. of nitrogen was present as albumin soluble in pepsin, of this but little is soluble in water, and with dilute acids, that containing 0·01 per cent. of hydrogen chloride produced the maximum of solution, which was but little greater than with water alone; the acidified pepsin acted rather better, but slowly, slower than when bran was so treated.

With cotton seed meal containing 5·951 per cent. of nitrogen as albumin soluble in pepsin, a 0·05 per cent. solution of hydrochloric acid dissolved more than half the albumin, and with the addition of pepsin, the solubility increased as soon as the solution contained more than 0·03 per cent. of hydrogen chloride; solution was most rapid at 38—40°, and no difference was noted whether the time was 15 or 30 minutes.

With hay, containing 1·038 per cent. of soluble albuminoïd nitrogen, if the solution contained 0·05—0·2 per cent. of hydrogen chloride, then 100 c.c. of this solution had no more solvent action than 50 c.c.; the most advantageous temperature was 40°, and 30 min. or 60 min. heating produced like results.

Experiments were made as to the preservation of milk with thymol, chloroform, and salicylic acid; thymol was found to be preferable.

E. W. P.

Oxidation in the Blood. By F. HOPPE-SEYLER (*Zeit. physiol. Chem.*, **14**, 372—376).—S. Handler (Abstr., 1889, 1225) and Yeo (*J. Physiol.*, **6**, 93) both state that in solutions of oxyhæmoglobin in sealed tubes, reduction ("self-reduction") does not occur without the presence of septic agencies, and in making this statement suppose that they are at variance with Hoppe-Seyler (*Zeit. physiol. Chem.*, **1**, 125), who now

writes to say that his words have been misunderstood, that he also considers that the reduction is due to septic agencies, that he always considered this to be the case, and that to his knowledge, he has never employed the expression "self-reduction." Reducing substances do not exist in the circulating blood (*Med. Chem. Untersuch.*, **1**, 123); this statement was first made 25 years ago, at a time when nearly all physiologists believed that a good deal of oxidative (metabolic) change occurred in the blood itself, and was the first important step made in the recognition of the true function of the blood as a carrier of indifferent oxygen. W. D. H.

Myohæmatin. By C. A. MacMunn (*Zeit. physiol. Chem.*, **14**, 328—329).—A reply to Hoppe-Seyler's criticisms (Abstr., 1889, 1231), in which the author maintains his original view that myohæmatin is a distinct and special pigment of muscle. In a foot-note, Hoppe-Seyler states that his opinion that the only pigment of muscle is hæmoglobin is also unchanged. W. D. H.

Fat of Bone-Marrow. By P. Mohr (*Zeit. physiol. Chem.*, **14**, 390—394).—C. Eylert (*Wittstein's Vierteljahrschrift f. pract. Pharm.*, **9**, 330) described in ox bone-marrow a new fatty acid of the formula $C_{21}H_{42}O_2$, melting at 72·5°, which he called medullic acid; the fatty acids present being palmitic acid, 46; medullic acid, 10; and oleïc acid, 44 per cent. As nothing further has been discovered as to the properties or salts of this acid, it was thought necessary to re-investigate the matter. The fatty acids were separated in the usual way, and the hypothetical acid was found on elementary analysis, and by examining its other properties, melting point, compounds, &c., to be nothing but stearic acid; the acids in the marrow-fat being present in the following proportions: palmitic acid, 22; stearic acid, 10; and oleïc acid, 63 per cent. Volatile fatty acids were absent in the fresh marrow. W. D. H.

Amount of Nitrogen in Cow's Milk. By L. F. Nilson (*Bied. Centr.*, **19**, 101—102).—A large number of nitrogen determinations were made in the milk of a cow fed with herring-cake. The maximum percentage of nitrogen was, in 1887, 0·492, the minimum, 0·465; in 1889, the maximum was 0·533, and the minimum 0·509. In the milk of another cow, the maximum was 0·504, and the minimum 0·483 per cent. of nitrogen. The amount of nitrogen in the milk of a cow remains, therefore, almost the same when the feeding is the same.

N. H. M.

Changes in Milk by Udder Tuberculosis. By V. Storch (*Bied. Centr.*, **19**, 105—109).—The author previously showed that the milk from glands attacked by tuberculosis becomes thinner and thinner until it loses entirely the appearance of milk; the change is accompanied by a continuous diminution in the amount of fat and sugar, and the milk gradually becomes alkaline. The relation of the mineral constituents also changes, the calcium phosphate diminishing and the soda increasing in quantity; the minerals of the milk from the healthy glands remain normal. In the advanced stages of the

disease, the milk acquires the appearance of blood-serum, which it also resembles in chemical composition.

The following results show the percentage composition (I) of the milk of the diseased glands, (II) of the milk of the healthy glands of the same cow, (III) of normal milk, and (IV) of cow's blood-serum:—

	Water.	Fat.	Total Albuminoïds.	Albumin.	Milk-sugar.	Ash.
I.	93·64	0·12	5·22	1·20	—	1·02
II.	74·30	11·79	11·59	2·39	0·40	1·01
III.	88·24	3·18	3·02	0·43	4·78	0·78
IV.	90·77	0·08	8·25	3·89	—	0·76

The percentage composition of the ash was:—

	Ca.	K_2O.	Na_2O.	$MgO + Fe_2O_3$.	P_2O_5.	Cl.
I.	7·52	5·08	42·37	0·79	8·76	44·64
II.	19·24	12·64	21·79	2·10	22·22	27·99
III.	21·93	25·31	9·94	2·87	28·69	13·73
IV.	1·59	3·20	54·85	0·70	3·35	46·87

The last numbers (ash IV) are those obtained by Bunze with bullock's blood-serum.

The milk from the healthy glands behaved like normal milk when heated, whilst that from the diseased glands formed a compact, gelatinous mass when heated at 100°; and very dilute acetic acid gave a precipitate which dissolved in a slight excess of acid.

It is probable that, during the disease, the tissues of the glands are gradually destroyed, and that, as the secretion of milk diminishes, it becomes replaced by blood-serum. The analytical results indicate that the caseïn and most of the fat of milk are derived from the globulin of the blood, and that the milk-albumin and the milk-sugar have also a common origin, to be looked for in the serum-albumin of the blood. N. H. M.

Secretion of Calcium Carbonate by Animals. By R. IRVINE and S. T. WOODHEAD (*Proc. Roy. Soc. Edin.*, **16**, 324—354; compare Abstr., 1889, 429).—Various calcium salts were given to hens, and it was found that the shells of the eggs laid were invariably normal, containing mere traces of phosphate and sulphate. With the exception of carbonate, the most favourable results were obtained with calcium phosphate; it, therefore, appears that all calcium salts are converted into phosphate, and in the secreting surfaces of the oviduct are converted by nascent or combined carbonic anhydride into carbonate. Compounds of strontium and magnesium, although analogous to those of calcium, were incapable of being formed into shells, and the eggs were only covered by strong membrane.

The remaining and principal portion of this paper is physiological, the experiments being conducted on crabs in sea water. As regards the parts of chemical interest, the summary shows that sufficient calcium carbonate for the formation of two shells can be stored up in the crop and gizzard; in the alimentary canal, calcium sulphide and

then calcium phosphate or chloride or lime soaps may be formed. The lime is carried as a soluble calcium sodium phosphate, as calcium chloride, or as a soap to the oviduct; it is there secreted along with urea, ammonium carbonate, carbonic anhydride, which latter combining with the lime in presence of urea, we have calcium carbonate deposited in the membranes, and the shell is formed of insoluble carbonate. In certain eggs the carbonate of soda is partially replaced by phosphate, and it is probable that a similar process occurs in marine animals which have the sulphate presented to them in presence of sodium chloride. Crabs, even in presence of sodium chloride, do not assimilate calcium sulphate, and those which throw off their shells in artificial sea water, containing no calcium chloride, do not form a new exo-skeleton of carbonate: as soon, however, as the chloride is added, although the sulphate be withheld, the shell formation may go on. Phosphates of the alkalis and alkaline earths occur in blood and lymph, and they act as carriers of lime, &c., to every point of the body where carbonic anhydride may be given off; thus carbonate is formed, and the phosphoric acid re-enters the circulation.

When alkaline phosphates associated with lime and albumin preponderate in the blood, the lime so separated is in the form of phosphate, as in bone formation; when these are partially replaced by an excess of alkaline carbonates as in marine animals, the lime is secreted as carbonate.

The corals have a secreting layer of cells which produce chitin, chitin infiltrated with calcium carbonate, and almost pure carbonate, with a small quantity of organic cementing material.

The carbonate may be formed by the ammonium carbonate produced by the decomposition of the effete products of animals, as urea, &c., decomposing calcium sulphate with the formation of carbonate.

E. W. P.

Ethyl Carbamate in the Alcoholic Extract of Normal Urine. By M. JAFFÉ and R. COHN (*Zeit. physiol. Chem.*, **14**, 395—404).—In analyses in which large quantities of urine were employed, an organic substance was found, which was easily soluble in water, alcohol, and ether, but which was different from any hitherto known constituent of urine. The present research was undertaken to determine its nature. After repeatedly treating the alcoholic extract of many litres of urine with various reagents, this substance was obtained in a crystalline form, and its reactions, and the results of elementary analysis, showed that it was identical with ethyl carbamate (urethane), $C_3H_7NO_2$. It was found to be constantly present in the urine of men, dogs, and rabbits, but in especially large quantities in dogs' urine, as much as 5 grams being on one occasion obtained from 7 to 8 litres.

The question then arises, whether this substance is present in the fresh urine, or is formed by the action of the alcohol on certain other constituents of that secretion. On *a priori* grounds, one would be inclined to suppose that it is absent from the normal secretion—first, because it is volatile and so would have passed off in the concentration to which the urine was subjected before it was treated with alcohol, and secondly, because large quantities of a powerful

narcotic could hardly be circulating in the healthy organism. This supposition was fully confirmed; if the extraction with alcohol were omitted, no ethyl carbamate was obtainable from the urine, although the same urine, after treatment with alcohol, yielded a large amount. Fresh diabetic urine and the fresh urine of a dog who had received large doses of alcohol by the mouth also yielded no ethyl carbamate.

What constituent of the urine is it, then, which gives rise to ethyl carbamate by the action of alcohol? It appears to be urea, which is acted on in this way—$CON_2H_4 + EtOH = NH_2 \cdot COOEt + NH_3$. By treating urea with hot alcohol, ethyl carbamate was obtained, together with a small quantity of another nitrogenous, crystalline substance, which was probably a similar compound of allophanic acid. The fact that urea is the source of the ethyl carbamate accounts for the quantity of the latter substance obtainable from dogs' urine, which is very rich in urea, being greater than that obtainable from human or rabbits' urine. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Chromogenic Functions of Bacillus pyocyanicus. By C. GESSARD (*Compt. rend.*, **110**, 418—420).—In ordinary cultivation fluids from beef or veal, *Bacillus pyocyanicus* yields a mixture of pyocyanin, which can be separated by agitation with chloroform, and another colouring matter which remains in the aqueous solution and imparts to it a green fluorescence. In egg albumin, the microbe develops no pyocyanin, but the green fluorescent substance is formed, and gradually changes, acquiring the brown colour of faded leaves. Even after repeated cultivations in albumin, however, the bacillus retains its power of producing pyocyanin in suitable media. Albumin which has been completely peptonised yields pure pyocyanin without any trace of the green fluorescence. The existence of both albumins and peptones in the ordinary cultivation fluids explains the production of both colouring matters. The fluorescence disappears on addition of acids, but returns on adding excess of alkali.

B. fluorescens liquefaciens and *B. fluorescens putridus* likewise produce a pigment in cultivation fluids from beef, or in albumin, but develop no colouring matter in solutions of peptones. Many other species seem to behave similarly.

Gelatin yields pyocyanin, like the peptones, but a greenish-yellow or greenish colouring matter is left in the liquid after agitation with chloroform, and gradually becomes red and then red-brown by oxidation. The new pigment can be obtained in a state of purity by adding 1 per cent. of glucose to the gelatin solution.

From these results it follows that one and the same microbe may develop different colouring matters in different media, whilst different species may develop the same colouring matter in the same medium.

C. H. B.

Germination of Jerusalem Artichoke. By J. R. GREEN (*Ann. Agron.*, **15**, 569).—During germination the tubers develop a ferment capable of transforming inulin into sugar. The ferment can be extracted from the tubers by glycerol; it is present in very small quantity, and only during germination. It can be artificially formed in the tubers not germinating, by heating them for 24 hours at 35°. Boiling destroys the activity of the ferment; thymol has no influence, so that bacteria are out of the question. It acts on inulin in neutral or very feebly acid solutions; alkalis and strong acids destroy it; it is not identical with dextrose; saliva is without action on inulin. The sugar formed does not crystallise, and reduces less readily than levulose or dextrose; there is produced at the same time an intermediate substance which is more soluble in cold water than inulin, dialyses more easily, and crystallises in pentagonal, rhomboidal, or elongated plates, or in needles arranged in tufts. Whilst inulin is insoluble in 65 per cent. alcohol, the new substance dissolves in alcohol of under 82 per cent. strength.

A good colour reaction for inulin is obtained on placing a microscopic preparation in an alcoholic solution of orcinol and then treating it with concentrated hydrochloric acid, when the inulin takes a bright orange-red colour. The sphero-crystals of inulin disappear during this process, but the place they occupied becomes red or orange. Inulin of commerce gives the same reaction, even in solution. When phloroglucinol is substituted for orcinol, the colour is brown.

J. M. H. M.

Occurrence of Boric Acid in Plants. By E. BECHI (*Bull. Soc. Chim.* [3], **3**, 122).—The ash of beech growing in the borax districts of Tuscany contains 1/30,000th of boric acid. T. G. N.

Intercellular Matter. By L. MANGIN (*Compt. rend.*, **110**, 295—297).—The author uses the term *intercellular matter* to denote the middle layer which connects the cells of soft tissues with one another. Its composition has hitherto not been accurately known.

The author's experiments show that in the Phanerogams and Cryptogams, with the exception of fungi and many algæ, the soft tissues consist of cellules connected by a cement of insoluble pectates. If the tissues are macerated with alcohol containing 20 to 25 per cent. of hydrochloric acid, and then in a solution of a normal potassium or sodium salt with an alkaline reaction, or in very dilute ammonia, or a solution of an organic ammonium salt, the pectic acid dissolves and can be separated from the insoluble tissues and precipitated from solution by the ordinary methods. The microscopic appearance of the tissues after various treatments is described in detail.

C. H. B.

Root Excretions and their Influence on Organic Matter. By H. MOLISCH (*Ann. Agron.*, **15**, 566—567; from *Sitzungsber. Akad. Wiss. Wien*, **46**, 84—109; compare Abstr., 1889, 68).—On suspending in water the roots of young seedlings of beans, peas, maize, &c., and adding potassium permanganate to the water, the colour is soon discharged; alcoholic tincture of guaiacum is turned blue; pyrogallol,

tannin, gallic acid, and humic substances also are oxidised; solutions of cane-sugar (1 in 1000) are inverted. In many cases the root secretion exudes in droplets; the viscous matter covering the young roots is really a gum and serves to ensure intimate contact between the root-hairs and particles of soil. J. M. H. M.

Composition of Fats of Fodder. By A. STELLWAAG (*Landw. Versuchs-Stat.*, 1890, 135—154).—The greater portion of this paper is occupied by extensive tables, showing the composition and characteristics of the fats of over 20 fodders, as regards the percentage of neutral fats, fatty acids (free and total), lecithin, stearic acid derived from lecithin, phosphorus, and unsaponifiable constituents. The melting points, saponification numbers, and molecular weights of the acids for each fat are also tabulated. E. W. P.

Chemical Composition and the Digestibility of the Proteïds of Various Grasses. By A. EMMERLING and G. LOGES (*Bied. Centr.*, **19**, 114—117).—20 different grasses were grown on the same ground, and each separately analysed. The soil was a loamy sand, containing (air-dry):—water, 1·25; humus, 3·27; nitrogen, 0·121; sulphuric acid, 0·018; phosphoric acid, 0·173; lime, 0·085; potash, 0·027; and magnesia, 0·008 per cent. The grasses were divided into two groups, I, very good, and II, good or of medium food-value. Group I included *Poa pratensis*, *P. nemoralis*, *Agrostis stolonifera*, *Festuca elatior*, *F. pratensis*, *Phleum pratense*, *Avena flavescens*, *A. elatior*, *Lolium perenne*, *Alopecurus pratensis*, *Dactylis glomerata*. The grasses of Group II were *Holcus lanatus*, *Anoxanthum odoratum*, *Poa compressa*, *Festuca ovina*, *Aira cæspitosa*, *Bromus arvensis*, *B. mollis*, and *Cynosurus cristatus*.

The average percentage composition of the grasses of the two groups was as follows (calculated on a percentage of water = 14·30):—

	Crude proteïn.	Pure proteïn.	Digestible proteïn.	Fat.	Carbo-hydrates.	Crude fibre.	Ash.	Digestibility coefficient of proteïn.
I.	7·77	5·38	4·70	1·45	36·77	32·66	7·05	60·06
II.	7·87	5·79	4·64	1·29	37·28	30·09	9·16	58·84

The results show that whilst according to a botanical analysis the grasses of Group I would be considered preferable to those of Group II, there is but little difference in the amount of food constituents and in digestibility. On the other hand, it is probable that a comparison of the grasses, if grown on different soils, would show considerable differences in chemical composition, so that hays of the same botanical composition might have different values as food, which can only be determined by chemical analysis. Chemical analysis is thus the simplest and most trustworthy method for determining the value of hay, but a botanical analysis is useful in separating the worthless or injurious grasses. N. H. M.

Lupulin. By E. STOCKBRIDGE (*Bied. Centr.*, **19**, 140—141; from *Agr. Science*, **3**, 29—35).—Hops grown in Japan from European

seeds are unsuitable for brewing. The amount of lupulin was only 9·13 and 5·84 per cent. in different years, whilst European hops contain over 12 per cent. Lupulin consists of volatile oil, hop-bitter, and hop resin. The amount of lupulin formed depends largely on the amount of sunshine during the ripening of the hops. In order to neutralise the injurious effects of rain, a manuring of potassium sulphate was applied; this raised the percentage of lupulin 1 per cent., but the amount produced was still only 7·19 per cent.

In analysing hops, it is not generally taken into account that only those portions are of any value for brewing which are soluble in water or alcohol, and that in good hops there is only a slight variation in the relation of substance soluble in alcohol to the substance afterwards dissolved by water. The results of 16 analyses showed this relation to be as 1 : 0·615 to 1 : 0·453; mean, 1 : 0·536. To find the amount of lupulin in a sample of hops it is only necessary to determine this relation and multiply it by 11·34/0·536. The number 11·34 is the average percentage of lupulin in good European hops.

N. H. M.

Constituents of Scopolia atropoïdes. By C. SIEBERT (*Arch. Pharm.* [3], **28**, 139—145).—The plant, a native of Germany, yielded a hyoscyamine aurochloride, a very small amount of atropine aurochloride, and still less of a mixture probably of hyoscine and hyoscyamine aurochlorides. A little scopoletin was also extracted, but not sufficient for analysis. The same remark applies to betaïn. Some choline was obtained, and its double chloride was analysed, but whether this substance occurs in the plant, or is produced by the decomposition of the lecithin contained therein, is doubtful. J. T.

Constituents of Anisodus luridus. By C. SIEBERT (*Arch. Pharm.* [3], **28**, 145—146).—This plant, belonging to the Solanaceæ, is found in the Himalayas. The plant in flower yielded a not inconsiderable amount of hyoscyamine aurochloride, whilst the plant taken after the ripening of its seeds yielded only a minute quantity of atropine aurochloride and no hyoscyamine aurochloride. The fresh flowering plant gave neither atropine nor hyoscyamine. J. T.

Chemical Composition of Molinia cœrulea (Mönch.) from Königsberg, near Raibl. By G. HATTENSAUR (*Monatsh.*, 11, 19—21).—On the heights near Königsberg, *Molinea cœrulea* grows on a soil containing large quantities of zinc glance and of galena, and the eating of it has been known to cause death to animals.

The air-dried grass contained 16·765 per cent. of water, and yielded 2·245 per cent. of ash having the following composition:—

	SiO_2.	PbO.	CuO.	Fe_2O_3.	MnO.	ZnO.
Calculated on the ash, per cent.	28·656	2·041	0·266	1·419	0·222	0·265
Calculated on the air-dried plant, p. c...	0·646	0·046	0·006	0·032	0·005	0·006

	CaO.	MgO.	K_2O, Na_2O.	SO_3.	P_2O_5.	CO_2.
Calculated on the ash, per cent.	1·418	1·322	57·871	2·528	3·194	0·798
Calculated on the air-dried plant, p. c. ..	0·032	0·298	1·027	0·057	0·072	0·018

On proximate analysis, the grass yielded the following percentages:—Crude fibre, 36·367; crude proteïn (N × 6·25), 6·175; crude fat, 2·070; ash, 2·245; non-nitrogenous extractive matter, 53·143. Substances soluble in water:—Inorganic salts, 1·768; organic constituents, 11·911. G. T. M.

Chemical Composition of Cultivated Strawberries. By W. E. Stone (*Bied. Centr.*, **19**, 117—119; from *Agr. Science*, 1889, 257—261).—The quite ripe fruit was dried in the sun to prevent loss of sap before being analysed; but the sugar and free acids were determined in the fresh substance. The following numbers form the means from analyses of 20 varieties cultivated in America:—

Dry substance.	Free acid.	Glucose.	Glucose after inversion.	Sugar (difference).
9·48	1·37	4·78	5·46	0·58 per cent.

The dry substance contained, per cent.:—

Ash.	Crude fibre.	Extracted by ether.	Albumin.	Non-nitrogenous extract.
6·53	16·35	6·75	10·51	60·79

The predominant acid is malonic acid; tartaric acid could not be detected, and citric acid can only be present in small quantities if at all.

European strawberries contain—water, 87·66; glucose, 6·28; and free acid, 0·93 per cent.; the dry substance containing—proteïn, 4·63; cellulose, 18·79; and ash, 6·56 per cent. They contain, therefore, more sugar and cellulose and less acid and proteïn than American strawberries. The relation of acid to sugar is, in wild strawberries, as 1 : 2, in American varieties as 1 : 3·5, and in European as 1 : 9. N. H. M.

Chemistry of Truffles. By A. Chatin (*Compt. rend.*, **110**, 376—382).—The author has analysed truffles grown in the soils of various localities. The proportions of dry solid matter varied from 20·84 to 24·26 per cent.; the proportion of ash in the solid matter varied from 5·62 to 9·88 per cent., and the proportion of nitrogen from 3·98 to 7·16 per cent. The chief constituents of the ash are silica, from 10·0 to 35·25 per cent., phosphoric anhydride, 18·45 to 30·25 per cent., and potassium oxide, 17·40 to 28·34 per cent. Sulphuric acid and calcium are also present in important quantity, and chlorine, iodine, magnesium, sodium, iron, aluminium, and manganese occur in small quantities. C. H. B.

Cultivation of the Leguminosæ. By E. Bréal (*Ann. Agron.*, **15**, 529—551; compare Abstr., 1888, 1330, and 1890, 79).—A detailed account of the author's recent experiments on the assimilation of nitrogen by leguminous plants and the relation of the root tubercles to this phenomenon. The roots can be inoculated with bacteria from other plants of the same family, and the plants thus inoculated will assimilate nitrogen from the air. The spores of these bacteria in water survive exposure to the frost of winter without losing their power of growth when inoculated on to roots the following spring. Peas inoculated with the bacteria of lucerne and cultivated in water containing only potassium chloride and calcium phosphate produced plants containing 17 times as much nitrogen as the seeds sown. A pea grown in water in a glass tube of small diameter produced a remarkable development of tubercles, especially near the junction of stem and root; the alternation of wetness and dryness in this situation seemed to favour the development of the tubercles. When peas, the roots of which were inoculated with the bacteria, were grown in three different-sized pots containing increasing weights of river gravel, it was found that the quantity of nitrogen fixed by the plant increased with the quantity of gravel in which it was grown. The gravel itself was not enriched in nitrogen when the quantity taken was small; probably the excessive aëration of the soil in this case is unfavourable to the fixation of nitrogen. Two Spanish beans inoculated with the bacteria of cytisus accumulated 16 times the nitrogen of the seed; the 10 kilos. of gravel in which they were grown contained at the beginning no nitrogen, and in the end 0·0581 per 1000. A plant of lucerne, grown from a piece of root furnished with tubercles, contained, on June 10, 43 times the nitrogen in the root sown; the gravel had increased by $\frac{7}{100}$ its original nitrogen. A second plant of lucerne, planted in October in 4 kilos. of gravel, gave the following year three cuttings containing 80 times the nitrogen in the piece sown; the nitrogen in the soil had more than doubled.

J. M. H. M.

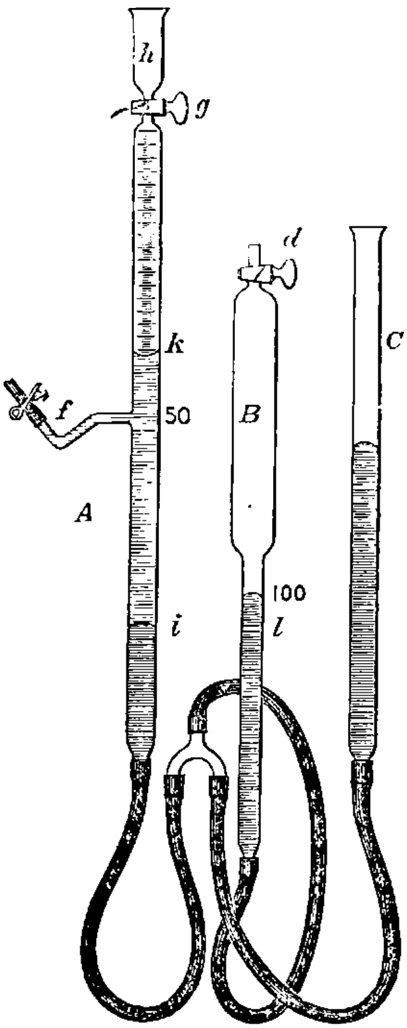
Analytical Chemistry.

The Gasvolumeter. By G. Lunge (*Ber.*, **23**, 440—449).—Many methods have already been devised for avoiding all reduction-calculations in gas analyses where the volume of the gases to be measured has to be compared with other gas volumes, but up to the present time no plan has been proposed for effecting the same thing where the gas is obtained from solid or liquid substances. The author has now succeeded in devising an apparatus in which the difficulties of the latter case appear to have been successfully overcome.

The principle on which the method rests is as follows:—The measuring tube for the gas is connected by means of a T-joint and very thick-walled indiarubber tubing with a movable "pressure-

tube," and also with a third tube termed the "reduction-tube," in which is placed such a volume of air that, when it is compressed to the division 100, it corresponds with 100 (or 50) c.c. of dry air at 0° and 760 mm. pressure. The liquid employed in the apparatus must in all cases be mercury. When the gas has been collected in the measuring tube, the other tubes are so placed that the mercury in the reduction-tube stands at 100, and also that the top of the mercury in the measuring-tube is level with that in the reduction-tube. The gases in both tubes are then under the same conditions, that is, the volume in each corresponds with that of the dry gas at 0° and 760 mm.

As an example of the detailed application and the method, the apparatus for the estimation of nitrogen in organic substances may be described. In the accompanying figure *A*, *B*, and *C* represent the



measuring, reduction, and pressure tubes respectively. The stopcock *g* is best so constructed that *A* may be connected with the vessel *h*, or either of these with the side tube shown; the tube *A* should further be of exactly 50 c.c. capacity from the stop-cock to just below the side tube *f*. A calculation is then made, once for all,

to find what volume 100 c.c. of dry air at 0° and 760 mm. would occupy under the conditions of temperature and pressure existing at the time of the calculation, due allowance being made for the vapour-tension of the potash solution used in the analysis. A small drop of the latter is passed into *B*, and then the exact quantity of air found by the above calculation admitted and the stop-cock *d* closed.* A volume of air is thus once for all enclosed which, at 0° and 760 mm., must, in the dry state, occupy 100 c.c.

Before commencing an analysis, the tube *C* is raised in order to fill *A* with mercury, and then exactly 50 c.c. of potash solution (sp. gr. 1·36) passed in; after which the analysis is conducted in the usual manner, the tube *C* being lowered to avoid any excessive pressure. When the gas has cooled, the tubes *B* and *C*, which are best held in spring clamps, are raised or lowered until the mercury in *B* stands at the 100th division. In this special case the mercury in *A* and *B* must not be brought to the same level, as allowance has to be made for the column of potash solution *ik*. If, as above suggested, 50 c.c. of solution having a sp. gr. of 1·36 ($\frac{1}{10}$th that of mercury) be taken, it is only necessary to fix a strip of paper, *l*, on the tube *B*, in such a position that the distance from the 100th division to the top of the strip is equal to $\frac{1}{10}$th of the length of the column *ik*, and then to bring the mercury in *A* level with the top of the strip *l*. (In ordinary working, this has proved quite easy of accomplishment, and does not require any previous practice.) The gases in *A* and *B* are then under exactly the same conditions, and the gas to be measured therefore occupies a volume equal to that of the dry gas at normal temperature and pressure.

As soon as the reading has been taken, the stop-cock *g* is so placed that the spent potash can pass off through the side tube, and a fresh quantity of 50 c.c. added, the apparatus being then ready for a further determination. In place of the usual graduation in c.c., the unit of graduation may be made 0·798 c.c., which corresponds with 0·001 gram of nitrogen; in this case, the weight of nitrogen to 0·0001 gram may be directly read off.

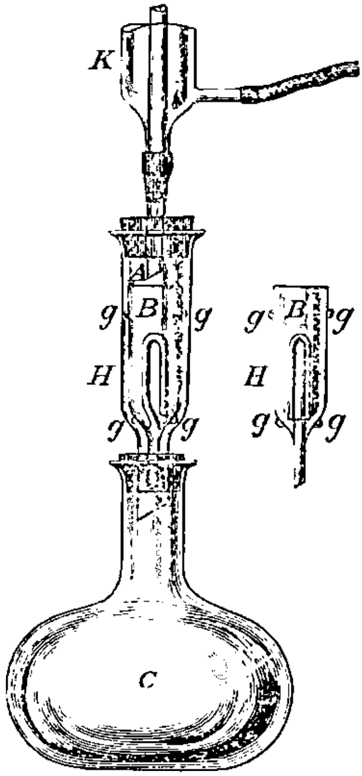
In the application of this improvement to such instruments as the nitrometer, &c., where the gases are saturated with moisture, the gas enclosed in the reduction-tube must likewise be saturated, and in the few cases where dry gases are measured, it must be dried over sulphuric acid. In all cases where the gas is collected directly over mercury, the level of the latter in the tubes *A* and *B* must be the same, no such correction being necessary as in the case considered above.

It is, of course, understood that the gases in *A* and *B* must have the same temperature, and when great accuracy is required, these may be surrounded by water, but in the majority of cases this is quite unnecessary.

H. G. C.

* This stop-cock may be replaced by a capillary tube, which is fused up when the necessary volume of air has been admitted. An accurately-ground and well greased stop-cock has, however, been found to hold equally well, and has the advantage that, if by chance gas of any kind should pass into *B*, the error may be readily corrected.

New Extraction Apparatus. By O. Knöfler (*Zeit. anal. Chem.*, **28**, 671—672).—This apparatus, whilst similar in principle to Soxhlet's, is of much simpler construction. The outer tube, *A*, is fitted tightly into the cork of the flask. The inner tube, *B*, lies loose within *A*, the two being kept apart by the projections *g*,*g*. The syphon may be either a bent tube or a straight tube with a cap. The substance to be extracted is placed on a filter-bed of cotton-wool



in the vessel *B*. The complete envelopment of the substance undergoing extraction by the vapour of the solvent maintains the liquid in *B* at its boiling point, and the absence of external tubes renders the apparatus less liable to injury than that of Soxhlet. M. J. S.

Rapid Detection and Estimation of Chlorine in Alkaline Thiocyanates. By C. Mann (*Zeit. anal. Chem.*, **28**, 668—669).—On mixing a thiocyanate with excess of copper sulphate and passing hydrogen sulphide, white cuprous thiocyanate is first precipitated. If the gas is stopped as soon as the precipitate begins to become brownish, and a further quantity of copper sulphate is added, the filtrate will be free from thiocyanate but will contain all the chlorine. For 5 grams of thiocyanate there should be used 20 grams of copper sulphate, each dissolved in 100 c.c. of water, with a subsequent addition of 8 grams of copper sulphate in 40 c.c. of water. M. J. S.

Detection of Nitrogen in Organic Compounds. By E. Donath (*Monatsh.*, **11**, 15—18).—The author finds that on heating organic compounds with excess of a saturated solution of potassium

hydroxide and powdered potassium permanganate, they are invariably partly converted into nitrons or nitric acid, which can be recognised by any of the usual tests. The reaction is exceedingly easy of application and very delicate: 0·03 to 0·05 gram of the nitrogen compound being sufficient in all cases at present tried. A method for quantitatively estimating nitrogen in organic compounds may probably be based on this method of detecting nitrogen. G. T. M.

Phosphorus Trichloride and Oxychloride. By G. DENIGÈS (*J. Pharm.* [5], 21, 216—217).—These two liquids are very similar in many of their properties, and a ready method of distinguishing between them is sometimes useful. If a good pinch of zinc powder is placed in a test-tube and one or two drops of the oxychloride are added (the zinc must be in excess), there is frequently an instantaneous production of flame; in all cases, on the addition of a little water, minute flames of hydrogen phosphide appear. With the trichloride, this reaction is not produced. J. T.

Magnesia in Calcium, Hydrogen, and Sodium Phosphates. By SCHLAGDENHAUFFEN (*J. Pharm.* [5], 21, 99—102).—The calcium salt, whether in the form of spangles or as large, transparent crystals, is known to contain up to 4 per cent. of calcium sulphate as an impurity. Careful search also reveals the presence of magnesia. The solution of sodium phosphate as usually prepared also contains magnesia in the form of a soluble phosphate. Hence, when the sodium salt is to be used for the precipitation of magnesia, it is necessary to prepare a mixture of the phosphate with ammonium chloride and ammonia, and to let this remain 24 hours before use, to afford time for the ammonium magnesium phosphate to form and settle. J. T.

Electrolytic Separations. By E. F. SMITH and L. K. FRANKEL (*Amer. Chem. J.*, 12, 104—112).—The solutions electrolysed contained usually rather less than 0·2 gram of each metal, and $4\frac{1}{2}$ grams of potassium cyanide in 200 c.c. of water; the current was usually of such a strength as to give 0·4 c.c. of mixed gases per minute in the water voltameter, and was allowed to pass for 16 hours.

Cadmium from Cobalt.—The separation is quantitative, the cadmium being completely deposited, and quite free from cobalt.

Cadmium from Nickel.—No good results were obtained, the deposited cadmium always containing nickel.

Mercury from Zinc.—The mercury is completely deposited, and contains no zinc.

Mercury from Nickel.—The mercury is completely deposited, and the separation is quantitative.

Mercury from Cobalt.—The results obtained at first were much too low, but when 3 instead of $4\frac{1}{2}$ grams of potassium cyanide were used, the mercury was completely separated.

Silver from Copper.—The silver is completely deposited. Former attempts with a much stronger current had been unsuccessful.

Silver from Zinc.—The silver is completely deposited.

Silver from Nickel.—The silver is completely deposited.

Silver from Cobalt.—The silver separates quantitatively if 3 grams only of potassium cyanide be used; with $4\frac{1}{2}$ grams it is not all deposited.

Copper from Cadmium in presence of Sulphuric Acid.—The separation of the copper was found to be quantitative when 10 or 15 c.c. of sulphuric acid (sp. gr. = 1·09) were present in about 200 c.c. of the solution, and the current gave 0·2 to 0·3 c.c. of mixed gases per minute. With a stronger current, cadmium was deposited along with the copper. C. F. B.

Estimation of Lead in Tin. By PERRON (*J. Pharm.* [5], **21**, 241—242).—An approximate method of estimating lead in tin consists in placing a drop of nitric acid on the tin, evaporating to dryness, and moistening the stain with potassium iodide solution. The intensity of the yellow coloration produced is supposed to give an indication of the amount of lead present in the tin. This is very misleading, as an experiment with Banca tin containing not more than 0·25 per cent. of lead shows, thus:—After evaporating off the acid, add some drops of water, then a little potassium iodide in powder, and quickly remove the excess of water by means of a pipette. A brown tint appears at once, due to the iodide, but after a few moments' agitation, a magnificent, yellow colour appears, which would be variously estimated as indicating 25 to 30 per cent. of lead. The test is somewhat improved by evaporating the stain several times to dryness, water being added each time, moistening with water, and laying a piece of filter-paper over the spot, on the moist part of which the iodide is laid. There is thus obtained a tint without admixture; but in spite of these precautions the depth of colour is always in excess of the lead really present. J. T.

Estimation of Copper by converting the Sulphide into Oxide. By C. HOLTHOF (*Zeit. anal. Chem.*, **28**, 680).—Quantities of about 0·2 gram of precipitated copper sulphide, filtered by suction, placed moist in the porcelain crucible, and ignited strictly according to Bunsen's instructions, are, at a moderate temperature, entirely converted, with incandescence, into oxide. If previously dried, the precipitate is partially converted into sulphate, and even after ignition for an hour at a temperature at which the crucible glaze fuses, traces of sulphate remain undecomposed. M. J. S.

Volumetric Estimation of Copper. By A. ÉTARD and P. LEBEAU (*Compt. rend.*, **110**, 408—410).—The estimation of copper by the action of stannous chloride on a strongly acid solution of cupric chloride is made difficult by the comparatively feeble colour of the cupric solution. Cupric bromide in presence of concentrated hydrobromic acid, however, has a deep purple colour, probably due to a hydrobromide of the cupric bromide (compare Denigès, Abstr., 1889, 747), and if this is gradually mixed with a solution of stannous bromide or chloride in concentrated hydrobromic acid, the disappearance of the colour, owing to the reduction of the cupric salt, gives a sharply defined end reaction.

The solution of the copper salt must be concentrated and mixed with excess of concentrated hydrobromic acid. Care should be taken to avoid unnecessary contact with air during titration, in order that the cuprous bromide may not be reoxidised, but it is not necessary to operate in an atmosphere of carbonic anhydride. A solution of stannous chloride in concentrated hydrochloric acid free from iron may be used instead of the solution in hydrobromic acid. The stannous solution must be titrated from time to time with a standard solution of copper. C. H. B.

Estimation of Mercury. By J. VOLHARD (*Annalen*, **255**, 255—256).—See this vol., p. 565.

Separation and Estimation of Tin and Titanium, with special reference to the Analysis of Silicates. By A. HILGER and H. HAAS (*Ber.*, **23**, 458—461).—The method of separation of tin and titanium given in this paper depends on the fact that when a mixture of stannic and titanic acids is acted on by hydrogen at a low red heat, only the former is reduced. After allowing the mixture to cool in the atmosphere of hydrogen, the tin may be extracted by boiling the mixture with 20 per cent. hydrochloric acid. The tin in the filtrate is then precipitated by hydrogen sulphide, the precipitate reduced by hydrogen, and oxidised by nitric acid to stannic oxide. The titanic acid is fused with 10 parts of potassium carbonate in a platinum crucible, treated with about 200 c.c. of water, and concentrated sulphuric acid added, drop by drop, until the potassium hydrogen titanate is completely dissolved. The solution is then neutralised with sodium carbonate, 2 grams of concentrated sulphuric acid again added, and the whole diluted to 400 c.c. After boiling for six hours, the titanic acid separates completely, and is collected, washed, ignited, and weighed.

In analysing minerals containing these acids, the finely powdered substance is mixed with water to form a thick paste, dilute sulphuric added until a thin liquid is obtained, and then fuming hydrofluoric acid, to eliminate silicic acid. The evaporated solution is treated with water, neutralised, 2 grams of sulphuric acid added, and the solution diluted to 400 c.c., boiled for six hours, and the precipitated stannic and titanic acids separated as previously described. The titanic acid precipitate sometimes contains iron, which may be removed by a second reduction in hydrogen and extraction with 20 per cent. hydrochloric acid. H. G. C.

Separation of Vanadic and Tungstic Acids. By C. FRIEDHEIM (*Ber.*, **23**, 353—357).—Great difficulty is experienced in the separation of vanadic and tungstic acids, especially in the analysis of vanadotungstic acid. Methods have been suggested by Gibbs (Abstr., 1884, 713) and by Rosenheim (Abstr., 1889, 762), neither of which are very convenient or accurate, and the author has therefore devised the following method, which gives satisfactory results. The concentrated solution of the salt is heated in a porcelain dish on the water-bath, a concentrated solution of mercurous nitrate, as neutral

as possible, added until the precipitate formed settles down well, and the free acid removed by digestion with mercuric oxide. The precipitate is collected, washed with water containing mercurous nitrate, and then, as far as possible, washed back into the dish, and evaporated until the whole becomes thick. It is next carefully triturated with very concentrated hydrochloric acid, warmed for five minutes on the water-bath, by which means the whole of the vanadium is converted into vanadyl chloride, and almost all the tungstic acid and mercury salts go into solution. The precipitate adhering to the filter-paper is also dissolved in hydrochloric acid and added to the above solution. On the addition of water, tungstic acid separates almost entirely, leaving vanadium and mercury in solution. After remaining for 24 hours, the precipitate is collected, washed with water containing small quantities of hydrochloric acid, dried, and ignited in a porcelain crucible, pure tungstic acid being obtained.

To isolate the vanadium, the solution is heated to 80°, hydrogen sulphide passed in until all the mercury is precipitated, the filtrate evaporated on the water-bath, oxidised with nitric acid, and again evaporated, this operation being repeated at least twice. The hydrated vanadic acid is dissolved in water containing nitric acid, evaporated in a platinum dish, the slight residue in the porcelain dish being dissolved in one or two drops of ammonia and added to the main portion; after evaporation, it is dried at 120° and heated in presence of air, but at first not sufficiently to cause fusion. The reddish-brown, crystalline vanadic acid obtained still contains 0·1 to 0·2 per cent. of tungstic acid, which may be estimated by treating the contents of the dish with dilute sulphuric acid and sulphurous acid, washing the residue with very dilute sulphuric acid and igniting. The vanadium solution may be evaporated, heated to drive off the sulphuric acid, and then ignited as before.

In the filtrate from the mercury salts, the dissolved mercury may be precipitated by hydrogen sulphide and the alkalis determined in the filtrate, the acid sulphate being converted into normal sulphate by Krüss's method (*Ber.*, **20**, 1682).

For the analysis of metatungstates by this method, these must previously be converted into ordinary tungstates by repeated evaporation with ammonia. Lead and silver salts are best decomposed by dilute solutions of chlorides of the alkali metals, and the remaining metallic salts by repeated fusion with sodium potassium carbonate, the aqueous extracts being neutralised with acetic acid and treated as above. The reagents employed must, of course, be pure, as any non-volatile impurity would remain in the vanadic acid, and cause the results to be inaccurate. H. G. C.

Water Analysis. By L. Vignon (*Bull. Soc. Chim.* [3], **3**, 2—4; compare Abstr., 1889, 1035).—Referring to his already published method, the author states that the distilled water used in making the test solutions should be boiled immediately prior to use, as otherwise the results are falsified by the carbonic anhydride dissolved therein (5 c.c. per litre). The precipitation of dissolved carbonates is best attained by ebullition in a porcelain or platinum dish for 15 minutes;

glass vessels should not be employed, since these determine an alkaline reaction. Any loss in volume resulting from this operation should be made up by the addition of previously boiled distilled water. T. G. N.

Estimation of Potassium and Humus in Soils. By J. RAULIN (*Compt. rend.*, **110**, 289—291).—The estimation of potassium is based on the fact that potassium phosphomolybdate is almost insoluble in water, whilst the phosphomolybdates of magnesium, sodium, calcium, iron, and aluminium are more or less soluble. The weight of the phosphomolybdate is 19 times as great as that of the potassium which it contains.

100 grams of ammonium molybdate, dissolved in a small quantity of water, is mixed with a solution of 6·5 grams of ammonium phosphate. Aqua regia is added, and the liquid is heated with successive additions of small quantities of aqua regia until the precipitated phosphomolybdate is completely dissolved. The liquid is then evaporated to dryness at 70°, and the residue treated with 400 c.c. of water and 5 c.c. of nitric acid, and the solution filtered.

A liquid for washing the precipitate is prepared by dissolving in 1000 c.c. of water 20 grams of sodium nitrate, and adding 2 c.c. of nitric acid, 20 c.c. of the phosphomolybdic solution, and 1·2 c.c. of a solution of 80 grams of potassium nitrate in 1000 c.c. of water. The liquid is heated, the precipitate allowed to settle, and the clear liquid decanted off.

A quantity of the soil containing about 15 milligrams of potassium oxide is dissolved in the usual way, and the greater part of the calcium, iron, and aluminium is separated. The substances left in solution are converted into nitrates, the liquid concentrated, acidified with nitric acid, mixed with 4·0 c.c. of phosphomolybdic solution for every 10 milligrams of potassium oxide present, and evaporated to dryness at 50°.

The residue is washed with 60 c.c. of the special solution and filtered through a tared filter, a counterpoise filter being washed with an equal volume of the wash-liquid. The precipitate is dried at 50° and weighed; wt. of ppt. × 5·2/100 = wt. of potassium oxide.

Humus in solution can be estimated by means of J. H. Smith's modification of the permanganate process. 10 c.c. of a solution of 16 grams of anhydrous manganese sulphate per litre is mixed with 10 c.c. of a solution of 10 grams of potassium permanganate per litre in a flask holding 250 c.c., and heated until the liquid is colourless and manganese peroxide is precipitated. Now add 100 c.c. of water, and 4 c.c. of a solution of sulphuric acid containing 150 grams of the monohydrate per litre, and then an exactly measured quantity of the humus solution, prepared by treating the soil with sodium hydroxide in the ordinary way. The quantity of humus must not be more than sufficient to reduce half the manganese peroxide present. Boil gently for eight hours in a reflux apparatus. Dissolve the unaltered manganese peroxide in a measured excess of decinormal oxalic acid, and determine the excess of oxalic acid by means of a standard solution of permanganate containing 1 gram per litre. The result gives

the quantity of humus in terms of oxalic acid, and from this the proportion of oxygen required for the complete oxidation of the humus can be calculated. The author gives an empirical table for the conversion of the oxalic acid equivalent into the corresponding quantity of humus. C. H. B.

Estimation of Petroleum in Turpentine. By W. M. BURTON (*Amer. Chem. J.*, 12, 102—104).—A balloon flask of 750 c.c. capacity is connected with a reflux apparatus, and also fitted with a drop funnel; 300 c.c. of fuming nitric acid (sp. gr. 1·4) is placed in the flask, and 100 c.c. of the turpentine to be tested is measured into the funnel. The flask is surrounded with cold water, and the turpentine is allowed to drop slowly into the nitric acid, when a violent action takes place, the turpentine being oxidised to various fatty and aromatic acids which are soluble in water, whilst the petroleum is scarcely affected. When the action is over, the contents of the flask are transferred to a large separating funnel, and treated with successive portions of hot water; the residual petroleum is measured, and represents the amount of the adulteration of the sample. Moderately accurate results may thus be obtained. C. F. B.

Impurities in Commercial Alcohol. By H. BORNTRÄGER (*Zeit. anal. Chem.*, 28, 670; compare Abstr., 1889, 552).—When a crude spirit, diluted to 30 per cent., is shaken with chloroform, the latter takes up amyl alcohol, acetal, aldehyde, and isobutyl alcohol, but leaves undissolved ethyl alcohol, acetic acid, normal propyl alcohol, and tertiary butyl alcohol, all of which may be present. Normal propyl alcohol is readily soluble in water, and leaves an agreeable fruity odour when rubbed on the hands. Isobutyl alcohol dissolves with difficulty, requiring 10 parts of water; it gives an unpleasant odour of fusel oil to the hands. If present in large proportion in alcohol, it produces a raspberry-red colour when 10 c.c. of the spirit is mixed with 3 drops of concentrated hydrochloric acid and 10 drops of aniline. M. J. S.

Mercury Nitrate as a Test for certain Aromatic Compounds. By P. C. PLUGGE (*Arch. Pharm.* [3], 28, 9—22).—The author has shown (this Journal, 1873, 533) that mercuric nitrate and the mercurous salt, as well as mixtures of the two salts, in presence of a very small quantity of nitrous acid, gives a red coloration with phenol. E. Millon (*Compt. rend.*, 48, 40) proposed the mixed salts as a test for albumin. R. Hoffmann (*Annalen*, 11, 123) proposed the same reagent as a test for tyrosine, but overlooked the necessity of a little nitrous acid. In the paper above cited, the author stated that the reagent was not only a test for phenol, but generally for those aromatic compounds containing a hydroxyl-group in the benzene nucleus. The present paper records the action of the test on 150 compounds, and the work is still in progress. It is, however, at this stage remarked that (1) the benzene-derivatives which do not contain hydroxyl do not give the reaction, or only give it after reactions which introduce derivatives containing hydroxyl;

(2) benzene-derivatives with a hydroxyl-group in the nucleus give the reaction. To this rule there are some exceptions, as the reaction is hindered when one or more of the hydrogen-atoms of phenol are replaced by other elements or by carbon-free radicles (for instance, Cl, Br, I, NO, NO_2, &c.). The reaction holds when the replacing radicle contains carbon. J. T.

Estimation of the Mineral Matter in Sugar. By J. v. GROBERT (*Chem. Centr.*, 1889, ii, 994; from *Neu. Zeit. Rub.-Zuck.-Ind.*, **23**, 181—182).—The author finds that the incineration of sugar may be assisted by the addition of oxalic acid, much in the same way that sulphuric acid assists this process.

The use of oxalic acid removes the objection to that of sulphuric acid, namely, the conversion of all the mineral matter into sulphates. If certain parts of the charred mass appear to glow less than the main portion, a little more oxalic acid may be thrown over these, which assists the combustion. J. W. L.

Estimation of Wood Fibre in Paper. By R. GODEFFROY and M. COULON (*Zeit. anal. Chem.*, **28**, 738—739).—Wood fibre, when boiled with a dilute solution of auric chloride, precipitates 14·285 parts of gold per 100 of purified, dry wood fibre. Cellulose has no such reducing action. To examine a paper, the weighed sample is treated first with cold, then with boiling water, for the removal of the size, then with a boiling solution of tartaric acid in 80 per cent. alcohol to dissolve out alumina, washed, dried, and extracted with alcohol and ether, and then treated with the gold solution.

M. J. S.

Estimation of Uric Acid in Urine by means of Sodium Hypobromite. By BAYRAC (*Compt. rend.*, **110**, 352—353).—Evaporate 50 c.c. of the urine on a water-bath, precipitate the uric acid by addition of 5 or 10 c.c. of hydrochloric acid of 20 per cent., and wash with alcohol in order to remove urea and creatinine. Dissolve the uric acid in a small quantity of sodium hydroxide solution and heat to 90° or 100° with 15 c.c. of a concentrated solution of sodium hypobromite. C. H. B.

Milk Analysis. By B. F. DAVENPORT (*Analyst*, 1889, 209—210).—For the estimation of total solids and fat, the milk is evaporated in flat-bottomed platinum basins, which for 5 grams of milk have a diameter of $2\frac{1}{2}$ inches at the bottom, thus giving a surface of 1 square inch for the residue from each gram of milk. With a residue of this thickness, the fat can be completely and readily extracted by boiling light petroleum, and its amount is known from the loss. It is recommended that the evaporation should be performed on a water-bath with closed top, as the absence of steam from the neighbourhood of the basins assists the evaporation materially. After weighing the butter-free residue, it is ignited in the same capsule for the determination of ash.

M. J. S.

Description of an Apparatus for drying Fodders containing Drying Oils. By O. FOERSTER (*Landw. Versuchs-Stat.*, **37**, 57—

62).—The percentage of oil obtained from foods containing drying oils is generally too low, because of the oxidation caused by drying the substance at a high temperature. The author has designed a drying apparatus which avoids oxidation, and which is here fully described. It consists of two chambers, the outer one holding water and hermetically sealed above, the only communication with the interior being that necessary for the water supply; the inner chamber is closed by a lid resting on a rim holding Wood's fusible metal, so that this chamber is also hermetically sealed. A pipe passes through the lid and conveys coal gas, which, passing out at the side near the bottom, supplies the burner for heating the water.

There are one or two modifications of this general design which can be used under varying circumstances; drawings are given of the various parts. E. W. P.

New Apparatus for the Analysis of Oils. By F. Jean (*Chem. Centr.*, 1889, ii, 1070—1071; from *Mon. Sci.*, **34**, 1211—1216).—For the determination of the melting point of fats, the author has constructed an apparatus in which an electric circuit is completed as soon as the fat melts. For this purpose, the fat, in the liquid state, is run into a U-tube and allowed to solidify. While still liquid, two platinum wires connected with the battery are passed one down each limb of the tube until they are opposite to each other. When the fat is solid, a little mercury is poured on to its surface in one limb. The tube is placed in a vessel of water, in which also the thermometer stands. The water is warmed carefully by means of a lamp placed underneath, and as soon as it is sufficiently hot to melt the fat, the mercury falls to the bottom of the U-tube, and connects the ends of the two wires with each other, thereby completing the circuit. In this there is also a bell placed, which indicates the exact moment when the fat melts.

For the determination of the amount of heat developed on mixing oils with sulphuric acid, the author has also constructed an apparatus. It consists of three parts. The innermost is a small, cylindrical bottle, having an internal tube from close to the bottom and reaching through the side near the top. By blowing through a mouth-piece, this bottle may be entirely emptied of its contents, which are thus forced through this internal tube into the next vessel. The latter is a beaker which contains the oil. The third part of the apparatus is a brass jar, in which the second vessel is placed, the space between the two being filled with wadding, as a non-conducting material. When making a determination, 15 c.c. of the oil is placed in the middle vessel, and 5 c.c. of concentrated sulphuric acid in the innermost one. The liquids are then brought to a temperature of 30° and vessels 1 and 2 placed in the brass outer vessel. The acid is now blown out of the innermost into the middle vessel, and the mixing performed by means of a thermometer.

For the determination of the index of refraction, the author has constructed a refractometer, in which the refractive effect of the oil under examination affects the size of the shadow in the field, which shadow is caused by the refractive power of a standard liquid or oil.

A scale is adapted so that the extent of alteration in the size of the shadow-half of the field may be recorded. J. W. L.

Estimation of Quinine in Quinine Tannate. By S. NEUMANN (*Zeit. anal. Chem.*, **28**, 663—668).—On examining, by Orrillard's method, some specimens of quinine tannate known to contain 25 to 30 per cent. of the alkaloïd, only about 7 to 13 per cent. was found. This results partly from the imperfect extraction by alcohol of the quinine contained in the residue of the evaporation with lime, and partly from the solubility of the alkaloïd in the potash employed to throw it down for weighing. The following method is proposed for technical purposes; it gives results which are about 3 per cent. above the truth:—2 grams of the powdered tannate is well shaken in a stoppered cylinder with 20—25 c.c. of aqueous potash of specific gravity 1·24. Care must be taken that the tannate does not adhere to the glass. Water is then added to make up to 60—80 c.c., and then 100 c.c. of ether, accurately measured. The cylinder is immediately closed and vigorously shaken. When the two liquids have separated, there must be no solid particles visible in either layer. 50 c.c. of the ethereal layer is taken out with a pipette and evaporated in a weighed beaker, the quinine being finally dried at 100° and weighed. An estimation can be completed in $1\frac{1}{2}$ hours. M. J. S.

Estimation of Chlorophyll in Leaves and in Extracts. By TSCHIRSCH (*Chem. Centr.*, 1889, ii, 996—997; from *Pharm. Centralhalle*, **30**, 611—614).—For the estimation of chlorophyll in leaves, a piece of leaf, cut as square as possible, is measured and then extracted with alcohol. The solution is acidified with one drop of hydrochloric acid, diluted to a certain volume, and a portion is then filled into a tube to the depth of 10 mm. In a second such tube, a standard solution of phyllocyanic acid in alcohol is placed, and the absorption spectra of the two solutions are compared by means of the spectroscope described by the author. The thickness of the standard solution is varied until band I appears of the same strength in each spectrum. In the case of the liquid under examination having a thickness of 10 mm., this band should appear faint; if the thickness be increased to 15 mm., it will appear dark in the middle, and band II will be just perceptible.

The standard phyllocyanic acid is prepared from grass by extracting with water and alcohol, and, after evaporating, the residue is warmed with hydrochloric acid. The beautiful, blue solution thus produced is phyllocyanin. It is filtered, the filtrate poured into water, the precipitate thus produced washed with water, and purified by treatment with alcohol, ether, and chloroform. It combines with zinc and copper.

The zinc salt may be used as a means of quantitatively determining the chlorophyll, the zinc precipitate containing 11·07 per cent. of the metal. J. W. L.

General and Physical Chemistry.

Refractive Indices of Saline Solutions. By B. WALTER (*Compt. rend.*, **110**, 708—709).—The author's experiments (this vol., p. 202) lead him to the conclusion that the refractive power of salts of the type $M''SO_4$ is 1·5 times as great as that of salts of the type M'_2SO_4, and three times as great as that of salts of the type $M'Cl$, a result essentially different from that obtained by Doumer (this vol., p. 433).
C. H. B.

Anomalous Rotatory Dispersion in Iron, Cobalt, and Nickel. By W. LOBACH (*Ann. Phys. Chem.* [2], **39**, 347—360).—Previous researches on the electromagnetic rotation of thin films of iron, &c., were directed principally to the determination of the maximum rotation and its dependence on the strength of the magnetic field. Kundt, in the course of his investigations, noticed that the dispersion in the case of iron was apparently anomalous, and the author, in the present paper, confirms this observation. The prism he employed was a direct-vision Wernicke liquid prism, and sunlight was always used in the experiments. The intensity of the magnetic field was 15,000 c.g.s. units, a strength sufficient to give the maximum rotation for the three metals investigated. The metallic films were deposited on glass plates either chemically or by electrolysis, and their thickness was estimated photometrically from the absorption they produced. They varied from 30×10^{-7} cm. to 100×10^{-7} cm. The results obtained are given below for the different wave-lengths as the simple rotation calculated for 1 cm. thickness—

	Liα.	D.	F.	G.
Iron........	223,000	195,000	145,000	122,000
Cobalt......	185,000	164,000	150,000	143,000
Nickel......	96,300	75,200	64,300	57,000

It is apparent from these values that the rotatory dispersion, not only of iron, but also of cobalt and nickel, is anomalous. J. W.

Dispersive Power of Aqueous Solutions. By P. BARBIER and L. ROUX (*Compt. rend.*, **110**, 457—460 and 527—532; compare Abstr., 1889, 805).—Examination of solutions of sodium, potassium, and barium chlorides, barium bromide, cadmium iodide, lead nitrate, chloral hydrate, sugar, citric acid, and aniline hydrochloride, with degrees of concentration varying from 8 per cent. to saturated solutions, showed that the dispersive power is a simple function of the concentration, but this does not hold for dilute solutions.

In solutions above a certain concentration, the excess of dispersive power, B, over that of pure water, b, is proportional to the quantity of dissolved substance, p, or $B - b = Kp$, K being a constant characteristic of each substance.

The value of the specific dispersive power B/d varies but little with the concentration, and is practically the same for all the substances examined, the minimum being 0·310 and the maximum 0·396. In the case of salts with a high dispersive power, however, the value is somewhat different.

If M is the molecular weight of the substance, $\frac{B - b}{p}M$ represents the *molecular increase of dispersion*, and is obtained by multiplying M into the coefficient K, which is constant for each substance. The mean value for chlorides of the type MCl is 0·020, the extremes being 0·021 and 0·019; for chlorides of the type $M''Cl_2$, the mean value is 0·044, the extremes being 0·050 and 0·038.

It follows that there is a simple relation between the relative dispersive power of a compound in solution and its chemical type and molecular weight. C. H. B.

Structure of the Line Spectra of the Elements. By J. R. Rydberg (*Zeit. physikal. Chem.*, **5**, 227—232).—The author, from a study of the wave-numbers ($n = 10^8\lambda^{-1}$, where λ is expressed in Ångström's units) of the spectra of the elements belonging to the first three groups of the periodic system, arrives at the following generalisations:—

1. The "long" lines in the spectra form pairs and triplets possessing the property that the wave-numbers of the corresponding components differ by a constant quantity, ν, for each element. Groups I and III have only double lines; Group II has triplets in addition.

2. The corresponding components of the pairs form series whose wave-numbers are functions of the successive natural numbers. Each series may be approximately represented by the equation $n = n_0 - \frac{N_0}{(m + \mu)^2}$. N_0 is a general constant for all elements and all series; n_0 and μ are constants for the special series; and m is the number in the series of the member considered. There are three kinds of series—principal, sharp (well-defined), and diffuse (ill-defined). The principal series form the most vivid lines in the spectra, and only occur in the first periodic group; next come the diffuse (really double) lines; and, lastly, the sharp lines. In the several groups the highest members are the weakest, as they are also in each series.

3. Series of the same group (diffuse or sharp) have the same value for μ; and series of the same order (1st, 2nd, and 3rd) have in the various groups the same value of n_0. A notation is given for the whole system of vibrations.

4. The wave-lengths and wave-numbers of the corresponding lines, and also the values of the constants (ν, n_0, μ) of the corresponding series are periodic functions of the atomic weights of the elements.

From the spectra of the neighbouring elements in the periodic system, the author calculates the wave-lengths of the lines of gallium, and finds a satisfactory agreement with the lines actually measured. He finally draws attention to the incompatibility of

his results with Lockyer's views as to the dissociation of the elements. J. W.

Absorption Spectra of Oxygen. By G. D. LIVEING and J. DEWAR (*Proc. Roy. Soc.*. **46**, 222—230; compare Abstr., 1889, I).—This is a continuation of the authors' experiments on the absorption spectra of oxygen and its compounds. The presence of nitrogen seems to reduce the absorption produced by oxygen of given tension. Variations of temperature (−100° to 100°) had very little effect on the absorption. Liquid oxygen was found to be equally constant with change of temperature, the bands above C, D, and F remaining the same for a range of temperature from −181° to above the critical temperature, so that liquid and gaseous oxygen have the same absorption spectra. The persistence of the absorption during condensation is remarkable, since the absorption spectrum is entirely changed when oxygen combines chemically. An examination of ozone gave only a general absorption with four faint bands at wave-lengths 1662, 1752, 1880, and 1990. The diffuse bands of oxygen at high pressures may be due to the presence of more complex molecules such as O_4, or to the constraint which the molecules experience during their encounters. With rise of temperature there is a slight weakening of the diffuse bands, a fact which supports the first hypothesis. The authors have re-examined the absorption spectrum of nitric peroxide, and confirm the conclusion of Bell (Abstr., 1885, 949) that this substance in the form of the molecule N_2O_4, whether liquid or gaseous, effects only a general absorption, and that the selective absorptions are due to the presence of the molecular form NO_2. H. K. T.

Maximum Polarisation of Platinum Electrodes in Sulphuric Acid. By C. FROMME (*Ann. Phys. Chem.* [2], **39**, 187—200).—Continuing his researches on the polarisation of platinum electrodes in sulphuric acid (Abstr., 1888, 390; this vol., p. 316), the author has studied the influence of the size of the electrodes on the polarisation. Electrodes of two different sizes were therefore employed, the first being foil of 1 sq. cm. surface and the second wire 0·3 cm. in length and 0·025 cm. in diameter, presenting a surface of 0·015 sq. cm. In order to overcome the difficulty arising from the fact that a small cathode becomes platinised in the course of the experiments, the cathode in every case, whether small or large, was coated with a thick layer of platinum black.

The experiments show that the polarisation alters rapidly with the size of the electrodes, increasing as the size of the cathode or of the anode decreases. Indeed, in very dilute solution, if a small cathode be taken, a polarisation value of 3·72 volts can be reached, using a large anode. Alteration in the concentration of the acid has least effect when large electrodes are taken, the difference between the highest and lowest value being about 0·78 volt, but if one or both of the electrodes are small, the greatest difference in the polarisation reached is very nearly double this number. If the electrodes are both small and the concentration of the acid be varied from 0 to 44

per cent., polarisation will be found at a maximum of 3·87 volts in a 32 per cent. solution, but with a 47 per cent. solution, it reaches its greatest attainable value of 5·5 volts. H. C.

Galvanic Polarisation of Platinum Electrodes in Dilute Sulphuric Acid with High Current Density. By F. RICHARZ (*Ann. Phys. Chem.* [2], **39**, 201—235). The author describes a method for measuring the polarisation after the polarising current has been interrupted, making use of the Helmholtz pendulum contact breaker. He finds that, employing platinum electrodes of small surface, the polarisation in dilute sulphuric acid never attains a value of more than 2·5 Daniells. The highest values were obtained for an intensity of about 0·001 ampère, whereas greater intensities gave smaller values for the polarisation, for instance, 2·4 Daniells with 0·4 ampère. This decrease is probably caused by heating of the solution. In the latter case also quantities of ozone, hydrogen peroxide, and persulphuric acid are formed, whereas not in the former, but it is evident that these do not exercise any great influence on the polarisation. H. C.

Electrical Conductivity of Air due to the Formation of Ozone. By J. ELSTER and H. GEITEL (*Ann. Phys. Chem.* [2], **39**, 321—331). —From the fact that the air in the vicinity of a bunsen flame is charged with ozone and conducts electricity, the authors were led to examine the electrical properties of the air enveloping a stick of moist phosphorus undergoing slow oxidation with formation of ozone. They found that the process of ozonising here also determined a similar assumption of conductivity by the air, but could not prove an electromotive force to be connected with it. The mere *presence* of ozone is not sufficient to impart conductivity to air, nor does the formation of solid particles of ammonium nitrite in the neighbourhood of the phosphorus exert any appreciable effect. When the formation of ozone is hindered by the presence of the vapour from oil of turpentine, the electric conductivity at once disappears.

Ozone was observed by the authors to be formed when a stream of air was passed over a platinum wire heated to whiteness by means of an electric current (compare Dewar, Roy. Inst., June 8, 1888). J. W.

Electrical Conductivity of some Solutions at Temperatures between 18° and 100.° By E. KRANNHALS (*Zeit. physikal. Chem.*, **5**, 250—258).—The apparatus used was similar to that described by Ostwald (Abstr., 1889, 4). The solutions examined were those of the chlorides and nitrates of sodium, potassium, and barium; potassium bromide, chlorate, and ferrocyanide; the sulphates of sodium and magnesium, and hydrochloric acid. The concentrations of the solutions varied from 1 gram equivalent per litre to 1 gram equivalent per 1000 litres. The results show that the higher the temperature the greater the increase in the molecular conductivity with rising dilution. The mean temperature coefficients are calculated for various dilutions, as also the values of μ_∞, the conductivity for infinite dilution at the temperatures 18°, 50·3°, 82°, and 99·4°. The

quotient μ_v/μ_∞ is found to decrease somewhat with rising temperature, from which the author concludes that the influence of temperature on the degree of dissociation of electrolytes which, at ordinary temperatures and in moderately concentrated solutions, are strongly dissociated, is only slight. The great increase in conductivity with the temperature is to be explained by the decrease in the viscosity of the solution. The author finally calculates the heats of dissociation by the method given by Arrhenius (Abstr., 1889, 1044), but his results are altogether at variance with those of the latter.

H. C.

Electrical Conductivity of Phenols and Hydroxybenzoic Acids. By D. BERTHELOT (*Compt. rend.*, **110**, 703—705). The solutions contained 0·01 gram-equivalent of the salts, &c., per litre, and the measurements were made with Lippmann's electrometer. The three hydroxybenzoic acids have different conductivities, the resistance increasing in the order ortho-, meta-, para-. The conductivity of the parahydroxybenzoic acid is practically identical with that of benzoic acid. When the acids are treated with 1 equivalent of sodium hydroxide, the numbers obtained are approximately the same in all three cases; the reduction of conductivity is $\frac{3}{4}$ for the ortho-acid, $\frac{7}{10}$ for the meta-acid, and $\frac{2}{3}$ for the para-acid. When a second equivalent of the alkali is added, the conductivities of the meta- and para-derivatives remain practically the same, but differ considerably from that of benzoic acid, since the second equivalent of alkali exerts an appreciable effect. A third equivalent exerts a smaller but still appreciable influence.

In the case of the ortho-acid (salicylic acid) the second and third equivalents of the alkali produce less effect than with the meta- and para-derivatives. The maximum difference in the case of salicylic acid is reached on addition of 1 equivalent of alkali, but in the case of the meta- and para-acids this maximum is given by the second equivalent. It follows that in the ortho-acid the phenolic function is less energetic than in the meta- and para-acids, a result which agrees with the thermochemical measurements of Berthelot and Werner.

C. H. B.

Development of Electricity and Heat in Electrolytes. By M. PLANCK (*Ann. Phys. Chem.* [2], **39**, 161—186).—Since the ions of an electrolyte are endowed with large electrostatic charges, it follows that before the electromotive forces become active a certain finite determinable amount of free electricity must be formed in the solution. A calculation of the forces necessary to cause a movement of electricity in an electrolyte is made in the present paper, starting with the assumption that in an electrolyte the ions are present in a fully dissociated condition. The passage of electricity from higher to lower potential gives rise to the development of heat, and the movement of the ions is also found to give rise to heating effects, since each ion carries a certain amount of heat with it, and, therefore, the accumulation of a number of ions in any particular portion of the solution will raise the temperature at that spot. H. C.

Electrolysis of a Mixture of two Salts in Aqueous Solution. By L. HOULLEVIGNE (*Compt. rend.*, **110**, 637—640).—Aqueous solutions of zinc and copper sulphates were electrolysed (1) with varying intensity of current and a constant difference of potential between the two electrodes, and (2) with constant intensity of current and varying difference of potential.

With a solution which contained, per litre, 37·5 grams of zinc and 0·963 gram of copper, the difference of potential being 6·94 volts, a variation from 0·0165 ampère to 0·0506 ampère caused a gradual increase in the ratio Zn/Cu from 1·15 to 5·64. With 48·1 gram of zinc and 2·30 of copper per litre, and a difference of potential of 7 volts, an increase in intensity from 0·0104 ampère to 0·0365 gave an increase in the ratio Zn/Cu from 0 74 to 1·58. It is obvious that the proportion between the deposited ions varies greatly with the intensity of the current, a result different from that obtained by Buff with hydrochloric and sulphuric acids. It is probable, however, that the electrolysis of mixed zinc and copper sulphates is complicated by secondary reactions, and if it is assumed that Buff's law is true, but that secondary action takes place between the deposited zinc and the copper sulphate, and is proportional to the time, it can be shown that the ratio Zu/Cu should increase with the intensity of the current.

With constant intensity of current, but a difference of potential varying from 3·25 to 6·55 volts, and from 2·85 to 5·26 volts, the ratio Zn/Cu remains the same except when the electromotive force approaches the minimum at which brass is deposited. C. H. B.

Electrochemical Effects on Magnetising Iron. By T. ANDREWS (*Proc. Roy. Soc.*, **46**, 176—193; compare Abstr., 1889, 92).—This is a continuation of the author's researches on the current produced when the opposite poles of two electrically connected magnets of approximately equal strength are immersed in solutions of various chemical substances. The general results obtained were that the north pole became positive to the south pole. In the present investigation, the solutions were applied to the upper ends of the magnets, as it was thought that the current produced in the previous experiments might have been due to the weakening of the submerged north pole, owing to its relation to the earth. It was found that the north pole was still positive, but that the electromotive force was slightly less than before. In both cases it was frequently observed that the south pole became momentarily positive at the commencement of the experiment.

H. K. T.

Influence of Temperature on the Magnetism of Salts of Metals of the Iron Group. By P. PLESSNER (*Ann. Phys. Chem.*, [2], **39**, 336—346).—The variation of the specific magnetic coefficient $K = A/M_2$ (A = magnetic attraction and M = intensity of field) with the temperature was investigated by a method depending on the torsion of a German-silver wire. Solutions of salts of metals of the iron group gave the following values for the constant α in the formula $K = K_0 + \alpha t$, the range of temperature considered being from 10° to 60°.

Ferric chloride........	α	$= -0.003542 \pm 0.000043$
Nickel sulphate	α	$= -0.003571 \pm 0.000014$
Cobalt nitrate	α_1	$= -0.003544 \pm 0.000094$
	α_2	$= -0.003567 \pm 0.000087$

These values are practically identical, so that we may take $\alpha = -\cdot 0035551 \pm \cdot 0000124$ as the general temperature coefficient for the above solutions.

Solid salts, on the other hand, have different coefficients. Thus, for hydrated manganous sulphate, $\alpha = -0.003114$; for the salt dried at 250°, $\alpha = -0.00269$; for cobalt sulphate dried at 250°, $\alpha = -0.00273$. The variation of the magnetic coefficient of nickel sulphate dried at 250° cannot be expressed by $K = K_0 + \alpha t$, but a sufficient approximation is obtained from the formula $K = K_0(1 + \alpha t + \beta t^2)$, where in one series of experiments $\alpha = -0.001504$ and $\beta = -0.00003324$.

J. W.

Allotropic Forms of Arsenic. By Berthelot and Engel (*Compt. rend.*, **110**, 498—499).—Crystallised arsenic, and amorphous arsenic obtained by the reduction of arsenious acid by hypophosphorous acid, were dissolved in bromine-water in a calorimeter. The quantities of heat developed at 7° (As = 75 grams) were as follows:—

Crystallised arsenic	+83·0 Cal.
Amorphous arsenic	+84·1 „

These numbers are almost identical with that obtained by Thomsen with crystallised arsenic at 18°, namely 83·7 Cal. Both forms of arsenic develop practically the same quantity of heat when converted into the same compound. The difference is of the same order of magnitude as in the case of graphite and the diamond, or crystallised and amorphous sulphur.

C. H. B.

Combination of Sodium and Potassium with Ammonia. By J. Moutier (*Compt. rend.*, **110**, 518—520).—A theoretical discussion of the observations of Joannis (this vol. p. 560).

Thermochemistry of Thiosulphates. By J. Fogh (*Compt. rend.*, **110**. 522—523, 524—525, 571—573, 709—711).—See this vol., pp. 694, 790.

Heat of Combustion of Rubidium. By N. Beketoff (*Chem. Centr.*, 1890, i, 308; from *Bull. Acad. St. Pétersbourg*, [2], **1**, 173—175).—The value for the heat of formation of rubidium hydroxide was determined by introducing the molten metal into a glass tube of known calibre, and when solid, a certain length was cut out, thus enabling the weight to be calculated. The tube, with the metal, was introduced into the calorimeter. By this means the metal was prevented from taking fire, and the reaction proceeded gradually. The author obtained the result, 164800 cal., which is very nearly the same as that for the formation of potassium hydroxide.

The heat of formation of rubidium oxide was determined by deducting the heat of formation of the hydroxide from the oxide,

from the heat of formation of the hydroxide from the metal. In order to prepare the oxide free from the peroxide, the mixed oxides obtained by oxidising the metal in absence of water were heated with sufficient metal to reduce all peroxide present to monoxide. The heat of formation of the hydroxide from the oxide was found to be 69900 cal., from which the heat of formation of the oxide is (164800 − 69900) = 94900. The heat of oxidation of the metals of the alkalis decreases gradually from lithium to rubidium.

J. W. L.

Heat of Combustion of Organic Isomerides. By I. OSSIPOFF *J. pr. Chem.* [2], **41**, 424—428).—The author compares the value for the heats of combustion of various organic acids, which he has recently calculated and published (*Compt. rend.*, **108** and **109**), with the values obtained by Stohmann (Abstr., 1889, 1097), and accounts for the differences in some cases.

He also points out that if Q_1 and Q_2 are the heats of combustion of two isomeric organic acids, Q_1 being greater than Q_2, k in the formula $[(Q_1 - Q_2)100] \div \frac{Q_1 + Q_2}{2} = k$, will be a constant in some cases, whilst in other cases it will be almost *nil;* thus, for maleïc and fumaric acids, $k = 2·5$; for teraconic and terebic acids, $k = 2·3$; for α- and β-diphenylsuccinic acids, $k = 2·4$; for α-nitrocamphor and phenonitrocamphor, $k = 2·6$; and for methylmalonic and succinic acids, $k = 2·2$.

A. G. B.

Neutralisation Phenomena of Aluminium and Beryllium Fluorides. By E. PETERSEN (*Zeit. physikal. Chem.*, **5**, 259—266).—Continuing his work on the heat of neutralisation of fluorides (this vol., p. 1), the author finds the heat of neutralisation of aluminium hydroxide with hydrofluoric acid to be 3 × 23415 cal.; the difference between this and that with hydrochloric acid being 3 × 4773 cal. The avidity of hydrofluoric acid towards aluminium hydroxide is three times as great as that of hydrochloric acid—as in the case of ferric hydroxide. The heat of neutralisation of beryllium hydroxide is given as $Be(OH)_2,2HFAq$ = 19683 cal.

H. C.

Heat of Hydration of Maleïc Anhydride. By I. OSSIPOFF (*Compt. rend.*, **110**, 586—588).—The dissolution of solid fumaric acid (116 grams) in dilute potash develops + 20·5 Cal.; the dissolution of solid maleïc anhydride in dilute potash develops + 31·6 Cal. Gal and Werner have shown that the heats of neutralisation by soda of fumaric and maleïc acids in solution are practically identical. Assuming that the same equality holds for neutralisation with potash, it follows that the hydration of maleïc anhydride with formation of maleïc acid develops + 9·6 Cal. If, on the other hand, fumaric acid is formed, the heat of hydration would be + 11·1 Cal. The difference 1·5 Cal., identical with the difference between the heats of dissolution, is too small to determine intramolecular changes when once hydration has commenced. It may become operative, however, if hydration is accompanied by exothermic changes, as in the action of a dissolved haloïd acid on maleïc anhydride.

C. H. B.

Berthelot's Law of Maximum Work and Spontaneous Endothermic Reactions. By R. COLLEY (*Zeit. physikal. Chem.*, 5, 242—249).—The author explains the exceptions to Berthelot's law of maximum work which are offered by spontaneous endothermic changes, on the assumption that any system which is not at rest may pass into some other less stable, but still possible, position of equilibrium with the production of negative work which is supplied by the energy originally stored in the system. The stability of a chemical compound depends, therefore, not only on the affinity or chemical attraction of the atoms for one another, but also on the distribution of the atomic energy among the different molecules. H. C.

Trough for Hofmann's Vapour-density Apparatus. By T. H. EASTERFIELD (*Chem. News*, 60, 250—251).—A disc of wood, turned to fit tightly into a retort-stand ring, is hollowed out so as to form an economical mercury trough and to support both the eudiometer and the steam-jacket. It is pierced by two holes, one opening within the steam-jacket, and fitted with a tube for the escape of the steam, the other opening without the steam-jacket and holding a tube to lead away the mercury into a receptacle beneath. D. A. L.

Determination of Vapour-density. By C. SCHALL (*Ber.*, 23, 919—924; compare Abstr., 1889, 331).—In this paper the author describes a simple form of apparatus for determining vapour-densities based on the principles already explained (*loc. cit.*). Instead of passing a measured volume of air into the apparatus, as was previously done, it is more convenient to decompose a weighed quantity of pure sodium carbonate and to compare the pressure of the carbonic anhydride produced with that of the vaporised substance.

If the weight of the substance is s, and that of the carbonic anhydride s', taking the specific gravity of carbonic anhydride compared with air under the same conditions as 1·529, the vapour-density of the substance is—

$$D = \frac{s}{s'} \times \frac{53}{22} \times 1{\cdot}529 \times \frac{k_6 - k_5}{k_5 - k_4},$$

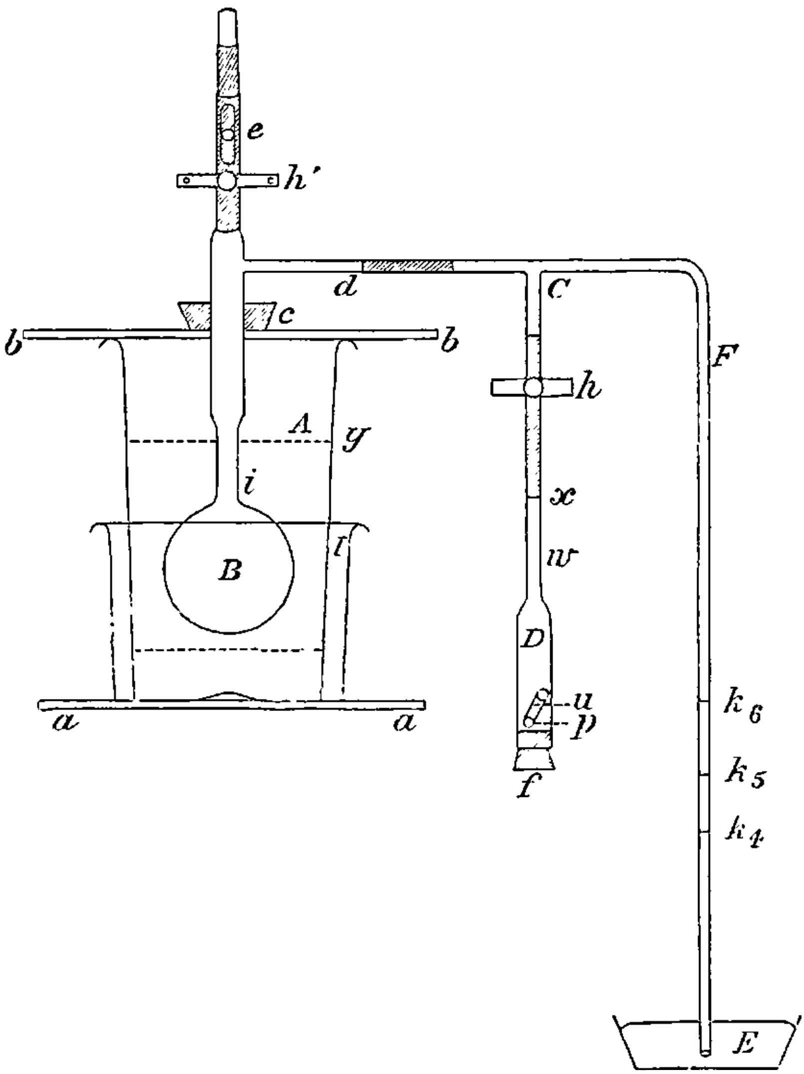
$$\text{or } \frac{s}{s'} \times 3{\cdot}682 \times \frac{k_6 - k_5}{k_5 - k_4},$$

where $\frac{k_6 - k_5}{k_5 - k_4}$ is the pressure-proportion of the carbonic anhydride to the vapour. Where $s = s'$, that is to say, when the weight of the substance is equal to that of the sodium carbonate employed, then $D = 3{\cdot}682 \times \frac{k_6 - k_5}{k_5 - k_4}$, so that it is only necessary to determine the pressure-proportion and the vapour-density is obtained by a very simple calculation.

The apparatus employed is shown in the following diagram:—

It consists of the heating space A, enclosed by a beaker, surrounding which, as shown in the figure, is placed the top half of a somewhat wider beaker, in order to prevent the cooling of

the heating vapour; with this arrangement, diphenylamine, and substances of even higher boiling point, can be quickly raised to the requisite temperature with a bunsen burner. The heating



substance is placed at the bottom of A, and if it be solid at the ordinary temperature, it should be carefully melted round the sides before placing the beaker on the heating plate *aa*. A flask B, the bulb of which is 150—200 c.c. in capacity, is suspended in the heating space by means of the cork *c*, which rests on the asbestos plate *bb*. The side tube *d*, which should be 100—110 mm. above the bulb, is connected by means of india-rubber tubing with the T-shaped tube C, one limb of which is continued to form the manometer F (internal diameter at the most 4—5 mm.), and dips into a vessel E containing mercury; three freely movable india-rubber rings k_6, k_5, k_4 are placed on the tube F. The other limb of the T-tube C is connected by means of india-rubber tubing to the narrow part *w* of the vessel D into which the small tube *u* containing the weighed quantity of sodium carbonate is pushed with

the india-rubber cork f before connecting D to C; the cylinder D also contains the dilute sulphuric acid (about 1 c.c.) which is introduced with the aid of a drawn-out glass tube. Above the bulb B the neck of the flask is drawn out, so that its internal diameter is not less than 5 or more than 20 mm.; the tube or sealed bulb containing the weighed quantity of substance is placed at e in a piece of closed india-rubber tubing and kept from falling by the pinchcock h'.

In carrying out a vapour-density determination, the stopcock h is opened, and, D being disconnected, the substance in A is heated in such a way that its vapour rises to about the level of y. As soon as the temperature is fairly constant, the mercury in F is raised as high as possible by suction with the mouth at x, and h is then closed; if the apparatus is air-tight, the mercury soon attains a constant level. The vessel D containing the sulphuric acid and the weighed quantity of sodium carbonate is then attached, h is opened, and the level of the mercury in F is marked with the ring k_6. The cylinder D is then inclined in such a way that the acid comes into contact with the carbonate, and by shaking repeatedly any bubbles of gas which remain in the small tube n are expelled; the level of the mercury is then marked with the ring k_5. The substance, previously placed at e, is now allowed to fall into B and the level of the mercury is marked with the ring k_4. Finally D is disconnected and h is opened; the whole operation requiring about 10 minutes after the apparatus has attained a constant temperature.

In a following paper the author will describe the methods to be employed in determining the vapour-density (1) under reduced pressure, (2) in an indifferent gas, and (3) in the case of substances which absorb carbonic anhydride.

Experiments with benzoic acid, naphthalene, phenol, aniline, nitrobenzene, and benzene gave good results, the heating substance employed being diphenylamine, ethyl benzoate, and, in the case of benzene, water.

F. S. K.

Molecular Volumes of Aromatic Compounds. By J. SAKURAI (*Chem. Centr.*, 1890, i, 425—426).—The author draws attention to the fact that if the molecular volumes of benzene and its homologues are calculated from the values given by Lothar Meyer and by Löschmidt for the molecular volumes of carbon and hydrogen, they do not agree with the molecular volumes as determined by experiment. He fixes the value of the carbon-atom in the benzene nucleus at 10·5, in the side-chain at 11, but the hydrogen-atom always at 5·5. The table (p. 684) allows of a comparison of the calculated and the determined molecular volumes.

The values calculated by the author for several benzene-derivatives containing oxygen also agree closely with those determined by Kopp, but he considers it somewhat premature to place too much dependence on such theoretical values, since so little is at present known of the influence of combination on the molecular volume.

	Calculated by		Found by	
	the Author.	Löschmidt.	Kopp.	Schiff.
Benzene	96	96	95·8	95·97
Toluene	118	114	—	117·97
Xylene	140	132	—	139·74
Ethylbenzene ...	140	132	—	138·93
Normal propyl-benzene	162	150	—	161·82
Para-ethyltoluene	162	150	—	161·94
Mesitylene......	162	150	—	162·41
Cymene........	184	168	183·5	184·46
Naphthalene....	149	147 or 153	149·2	—

J. W. L.

Dissociation of Amine Hydrochlorides and Salts of the Fatty Acids in Solution. By J. A. MULLER (*Compt. rend.*, 110, 588—590). —The dissociation of many salts in solution can be rendered evident by means of phenolphthaleïn. If a concentrated solution of an amine hydrochloride containing a small quantity of phenolphthaleïn is mixed with sufficient free amine to produce a rose colour, the liquid becomes colourless when diluted or when heated. In the latter case the colour reappears on cooling; in the former it reappears on addition of a further quantity of amine. These results show that when an amine hydrochloride dissociates, the action of the hydrochloric acid on the indicator is greater than that of the amine. Many bases, such as pyridine, picoline, lutidine, and hydroxylamine, show no similar phenomena, because their action on phenolphthaleïn is too feeble.

When phenolphthaleïn is added to solutions of the alkaline salts of the fatty acids, the liquids become alkaline when diluted or when heated, the action of the alkali on the indicator being in these cases greater than the action of the acid. In this way it is easy to show that in the case of salts of formic, acetic, propionic, normal butyric, and valeric acids, the amount of dissociation under given conditions increases with the molecular weight of the acid, a result which agrees with Berthelot's observation that the heat of formation in this series of salts decreases with the molecular weight of the acid.

Normal potassium and sodium salts of the strong inorganic acids gave no coloration when diluted or heated, and hence these salts do not dissociate.

C. H. B.

Rise of Solutions in Capillary Tubes and the General Law of this Phenomenon. By M. GOLDSTEIN (*Zeit. physikal. Chem.*, 5, 233—241; compare Abstr., 1889, 205).—The author finds that the law of vapour tensions and that of the rise of solutions in capillary tubes are similar in nature. If H represents the height of the rise of water and h that of the solution of a substance of molecular weight M, then $H - h/HM = C$, a constant which depends only on the percentage of dissolved substance. If the above expression be multiplied by Van't Hoff's coefficient, i, the law holds also in the case of electrolytes; this is shown by reference to experiments by the author

and by Valson. It is pointed out that the above law is in close relation to that ennunciated by Traube (Abstr., 1885, 116).

H. C.

Chemical Equilibrium between Hydrogen Chloride and Hydrogen in conjunction with Metals. By M. RIBALKIN (*Chem. Centr.*, 1890, i, 308; from *Bull. Acad. St. Pétersbourg* [2], **1**, 279—282).—The chemical equilibrium between copper and hydrogen chloride occurs at temperatures between 230° and 440°, but not at temperatures ranging from 100° to 230°; at 230°, 93 per cent., at 440°, 66 per cent., of the hydrogen chloride is decomposed.

In the case of hydrogen heated with cuprous chloride, no reaction takes place at 200°; at 230°, 5 per cent., and at 440°, 35 per cent. of hydrogen chloride is formed.

J. W. L.

Freezing of Colloïdal Solutions. By N. LUBAVIN (*J. Russ. Chem. Soc.*, **21**, 397—406).—The investigations of Pfaff, Geiger, and Payen on the freezing of colloïdal solutions have been overlooked by subsequent investigators of colloïdal solutions, especially Graham and Van Bemmelen. The author finds that from some of such solutions the substance dissolved is completely or partly separated after freezing, whereas in the case of others the precipitate again passes into solution. A solution of colloïdal silicic acid, obtained by mixing soluble glass with hydrochloric acid in aqueous solution, was divided into two parts, one of which was exposed to a temperature of 7—10° for two days, after which it was exposed to the temperature of the laboratory (+15°) for two days. From the frozen solution as much as 96·96 per cent. of the silica was separated by filtration, whereas the original unfrozen solution yielded only 0·72 per cent. of insoluble silicic acid. This is not in contradiction with Graham's statement, that the stability of a colloïdal solution of silicic acid increases with decreasing temperature, for, according to Graham, more concentrated solutions are more easily coagulated. Indeed, on freezing, gradual concentration takes place, owing to the separation of ice, so that the coagulation is accelerated. A colloïdal solution of antimony trisulphide was prepared by Schulze's method, namely, saturating a solution of 1 part of tartar-emetic in 200 parts of water with hydrogen sulphide. Nothing separated from the original solution, even when it was allowed to remain for months at the ordinary temperature; whereas from the same solution, after exposure to a temperature of −6° for 29 hours and subsequent thawing of the ice, complete separation of the antimony sulphide took place. When a very large quantity of the same solution was exposed to a low temperature, the separation was not quite complete. A colloïdal solution of copper sulphide was obtained by the action of hydrogen sulphide on copper glycollate. The separation of the sulphide was incomplete, although the solution was kept one day at −6° and one day at −19°. Nothing separated out at the ordinary temperature. Colloïdal solutions of ferric hydroxide, obtained by the dialysis of different preparations of basic chloride, sometimes remain uncoagulated by freezing, sometimes are partly coagulated. This depends on the purity of such solutious, and partly, perhaps, on the rate of cooling. Solutions of potassium ferric

tartrate behaved in a similar manner. One part of starch was dissolved in 100 parts of boiling water, and the solution was kept at a temperature below zero; flocks separated, as shown already by Payen, but the separation was incomplete. It was found that starch solutions which had been subjected to freezing are much more easily and quickly filtered than the same solutions not frozen, so that this process might be used for the better filtration of slimy liquids and precipitates. Neither white of egg nor milk is coagulated, even on freezing at $-15°$ to $-20°$. The fact that peat falls to pieces after being frozen is explained by the author on assumption that it contains colloïdal substances, which are coagulated by freezing. B. B.

Solubility and Heat of Fusion. By J. WALKER (*Zeit. physikal. Chem.*, 5, 193—197).—From the thermodynamical equation, $dp/dt = \rho/Tv$, and the gas-equation, $pv = 2T$, here applied to solutions, the author deduces a relation between the solubility of a substance in any solvent and its heat of fusion. T denotes the absolute temperature, p the osmotic pressure in the saturated solution, v the volume of the solution, and ρ the molecular heat of solution, which is assumed to remain constant within the interval of temperature studied. The determinations of solubility are made above and below the melting point of the substance. Calculating from the solubility of paratoluidine in water, 44·5 cal. was obtained as the heat of fusion of the latter, the value directly determined being 39 cal. For water (dissolved in ether) the heat of fusion, calculated on the assumption that the molecule of the dissolved water is H_2O, amounts to 154 cal., whereas experiment shows it to be 80 cal. If, however, it be assumed that the molecule of water dissolved in ether is H_4O_2, the calculation gives 77 cal., in agreement with the experimental value. This assumption receives support from the observation of Eykman (this vol., p. 324), that the depression of the freezing point produced by water in liquid paratoluidine has only half the normal value. J. W.

Solution-equilibrium of Thorium Sulphate and its Hydrates. By H. W. B. ROOZEBOOM (*Zeit. physikal. Chem.*, 5, 198—216).—Nilson and Krüss (*Ber.*, 15, 2519, and 20, 1665) have shown that when anhydrous thorium sulphate is dissolved in ice-cold water, and the solution warmed to 20°, large quantities of a sparingly soluble hydrate with $9H_2O$ separate. This observation might seem to indicate a stable solution of the anhydrous salt reaching its point of transformation into the above hydrate at 20°, in contradiction to the general rule that on increase of temperature the point of transformation into a lower hydrate, and not into a higher one, is reached. The author has investigated the phenomena in detail, and finds an explanation of the anomaly in the fact that the hydration and dehydration of thorium sulphate proceed at low temperatures with extreme slowness, so that solutions apparently stable with respect to the hydrate $Th(SO_4)_2,9H_2O$ are in reality not so, but undergo steady though slow changes of concentration. The solubilities of the anhydrous salt and of hydrates with 2, 4, 6, 8, and $9H_2O$ respectively are investigated, and the results are given both in tabular and curve form. J. W.

Inorganic Chemistry.

Prolonged Action of the Electric Discharge on Iodine. By C. LUEDEKING (*Chem. News*, **61**, 1—2).—The author has investigated the phenomenon of the disappearance of iodine and the appearance of hydrogen, when the former element is submitted to the spark discharge in hermetically sealed glass tubes. Firstly, he noticed a reduction of the volume of the gas contained in the tube, which he attributes to the disappearance of the oxygen of the air originally contained in the tube. Secondly, analytical results indicate that the iodine is still present, but in the form of iodides and, probably, iodates, these salts being formed at the expense of the bases in the glass; this would account for the etched appearance of the latter after the experiment. The author then shows that the hydrogen is introduced into the tube in the form of hydriodic acid retained by the iodine, and as the iodine ultimately all combines to produce iodides, the hydrogen is left, and "instead of an iodine tube we have a hydrogen tube developed." D. A. L.

Preparation of Hydrobromic Acid. By A. RECOURA (*Compt. rend.*, **110**, 784—785).—The ordinary methods of preparing gaseous hydrogen bromide are inconvenient, and the evolution of the gas cannot be readily regulated. The author proposes a method which is based on the fact that the action of gaseous hydrogen sulphide on liquid bromine with formation of gaseous hydrogen bromide and solid sulphur develops +14·4 Cal., without taking into account the heat developed by the combination of the sulphur with the excess of bromine.

Hydrogen sulphide is bubbled through a layer of bromine contained in a tall, narrow vessel and covered by a layer of water or hydrobromic acid. The gas passes into a second flask which contains a solution of potassium bromide in hydrobromic acid holding a small quantity of red phosphorus in suspension, and the gas which issues from this flask contains neither bromine vapour nor hydrogen sulphide. The current of hydrogen bromide is controlled by regulating the current of hydrogen sulphide. The latter gas should be made in a "continuous" apparatus. C. H. B.

Purification of Hydrofluoric Acid. By R. HAMILTON (*Chem. News*, **60**, 252).—The apparatus employed by the author for distilling commercial hydrofluoric acid consists of a heavy sheet-lead retort, 6 inches high and 4 inches in diameter, with a rim at the top formed by beating the lead over an iron ring 1 inch deep and $\frac{3}{8}$ inch thick; the lid is of $\frac{1}{4}$-inch iron plate, covered with lighter sheet lead, and is fixed down by a screw working in a socket in an iron bridge, which is secured to projections on the opposite sides of the iron ring of the rim. A washer of india-rubber is placed between the cover and the

rim. The leaden nose of the retort points upwards, and is connected by india-rubber tubing to a Liebig's condenser, the inner tube of which is of thin india-rubber. The retort is charged through a funnel with 25 per cent. hydrofluoric acid, which yields a distillate of convenient strength for analytical work. The first portions of the distillate contain silicate and are discarded, whilst any sulphur is removed by filtration. D. A. L.

Selenic Acid. By C. A. Cameron and J. Macallan (*Proc. Roy. Soc.*, **46**, 13—35).—The authors have prepared anhydrous selenic acid, H_2SeO_4, and compared its properties with those of sulphuric acid. The anhydrous acid was obtained by concentrating the aqueous acid over the water-bath and then heating it with agitation in a vacuum at 180° so long as acid distilled over. The residual acid crystallised on cooling, and contained 99·71 per cent. of anhydrous acid (Se = 78·87). Anhydrous selenic acid has a specific gravity of 2·9508, and melts at 58°, forming a colourless, oily liquid of sp. gr. 2·6083. The presence of a small quantity of water greatly lowers its freezing point, so that it does not solidify until cooled to −51·5°. It crystallises in hexagonal prisms. Tables of the specific gravities of the aqueous acid are given. Anhydrous selenic acid absorbs moisture with avidity, blackens organic matter, and decomposes glycerol, evolving acraldeyde. It reacts violently in the cold with phosphoric chloride, the products of the reaction being now under examination. It dissolves selenious anhydride, but does not in this way form an acid corresponding with the acid $H_2S_2O_6$. Selenic acid forms a monohydrate, H_2SeO_4,H_2O, melting at 25°. It can be obtained by boiling the aqueous acid until its temperature rises to 205°, and then dropping a crystal of the acid into the cooled liquid. Conclusive evidence of the existence of higher hydrates could not be obtained, but there is a considerable evolution of heat on diluting the monohydrate to a strength corresponding with the dihydrate, and a slight development of heat on the addition of more water. Selenic acid, when heated in a vacuum at 200°, decomposes into selenious anhydride, oxygen, and water. At ordinary pressures, the acid distils until a temperature of 260° is reached, when decomposition sets in.

Selenic acid does not dissolve sulphur at ordinary temperatures, but at 63° dissolves it with a deep indigo-blue colour; decomposition sets in at the same temperature with evolution of sulphurous anhydride. It dissolves selenium in the cold, producing a green solution which evolves selenious anhydride at 75°. Tellurium dissolves in selenic acid in the cold with a purple-red colour, but this soon disappears with production of selenious acid. It is probable that the above coloured substances are selenoxides, namely, $SSeO_3$, $SeSeO_3$, and $TeSeO_3$ respectively, analogous to the corresponding sulphoxides produced by dissolving the three elements in sulphuric acid.

Selenic anhydride could not be obtained by passing a mixture of selenious anhydride and oxygen over heated platinum sponge or by the action of ozone on selenious anhydride, but the above selenoxides seem to point to its possible existence. Anhydrous selenic acid, when mixed with phosphoric anhydride and heated at 100°, yields crystals on cool-

ing which on analysis give results agreeing with those of selenic anhydride. The substance is under examination. The selenates of antimony, bismuth, and platinum are described. H. K. T.

Catalytic Formation of Ammonia from Nitrates. By O. Loew (*Ber.*, 23, 675—680).—The author points out that, as almost all plants can utilise nitrates for building up the albuminoïds, and, as in the latter the nitrogen is partly in amidic, partly in imidic or tertiary union, a preliminary reduction of the nitric acid to ammonia must first take place. The physiological conversion of nitric acid into ammonia may be readily shown by allowing common putrefactive organisms to grow in a 1 per cent. peptone solution containing also 0·2 per cent. of potassium nitrate and a similar amount of potassium phosphate. In presence of air, the formation of nitrite may be observed within two days, and in two months the whole of the nitrogen is converted into ammonia. If air be excluded and 0·2 per cent. of alcohol and of sodium hydrogen carbonate added, the alcohol is oxidised by the oxygen of the nitrate, and gives up its hydrogen to the nitrogen, the products being ammonia and acetic acid. To explain this, it must be assumed that the living protoplasm, which is built up of extremely labile albuminoïds, is in a state of violent molecular agitation, and that the intense atomic motions are communicated both to the alcohol and to the nitric acid, with the result that the above-mentioned exchange takes place.

The author regards the activity of platinum-black charged with oxygen as due, not to the fact that the oxygen is so greatly condensed, but that the oxygen is in a similar state of violent molecular motion. He has, therefore, examined whether the reduction of nitric acid to ammonia may also be accomplished by its means. Pure dextrose and potassium nitrate were dissolved in water and heated for six hours at 60—65° with platinum-black charged with oxygen, and prepared by the method previously described (this vol., p. 453). A quantitative experiment showed that 45·6 per cent. of the nitrogen of the nitric acid had been converted into ammonia. In order to meet the possible objection that the dextrose is first oxidised to aldehydes or similar compounds, which then exert a reducing action on the nitric acid, dextrose solution was warmed alone with the same platinum-black under identical conditions, and the filtrate then digested with a little potassium nitrate. No ammonia could be detected in this case.

In this reduction, two processes take place together, namely, the oxidation of dextrose, in which the oxygen is gradually used up, and the reaction between dextrose and potassium nitrate, in which the oxygen acts merely from its peculiar mode of vibration, and is not absorbed.

If methyl alcohol be substituted for dextrose, it absorbs all the oxygen of the platinum-black so rapidly that only traces of ammonia are formed.

Naegeli, in 1879, in his theory of fermentation, supposes that the latter is due to the transmission of a peculiar kind of molecular motion from the living protoplasm of the yeast to the sugar molecule.

The author points out that Naegeli's ideas may also be applied to many other processes which take place in the cells, and that even the most remarkable of the changes which occur there, namely, the formation of carbohydrates from carbonic anhydride, is very likely to be due to the transmission to the latter of a molecular motion compounded of the vibrations of the living material and of the light absorbed by the chlorophyll. H. G. C.

Oxidation of Hypophosphorous Acid by Spongy Palladium. By R. ENGEL (*Compt. rend.*, **110**, 786—787).—Contrary to the statements of Wurtz and Graham, palladium precipitated from a solution of the chloride by means of hypophosphorous acid retains a small quantity of hydrogen. The author observed that the quantity of hydrogen evolved was much greater than the quantity which could be liberated from a palladium hydride. Further investigation showed that when spongy palladium is brought in contact with hypophosphorous acid, the latter is rapidly converted into phosphorous acid, and hydrogen is liberated. The palladium seems to retain its activity indefinitely, and 0·5 gram of the metal decomposed the acid obtained from 500 grams of barium hypophosphite. The reaction is not arrested by pressure.

Berthelot has shown that the conversion of hypophosphorous acid into phosphorous acid is exothermic. It is probable that the palladium removes an atom of hydrogen from the hypophosphorous acid, but quickly loses it, whilst the residue of the acid interacts with the water, combining with hydroxyl, and liberating another atom of hydrogen. C. H. B.

Combination of Hydrogen Phosphide and Ammonia with Boron Chloride and Silicon Sesquichloride. By A. BESSON (*Compt. rend.*, **110**, 516—518).—Hydrogen phosphide combines with boron chloride with development of heat, and yields the compound BCl_3,PH_3, a white solid which alters rapidly when exposed to air, and is immediately decomposed by water with liberation of hydrogen phosphide. It begins to dissociate at 20° under the ordinary pressure, and if the products of dissociation are slowly cooled, the compound is obtained in bulky, colourless, highly refractive crystals.

Ammonia displaces the hydrogen phosphide from this compound at 8°, and yields the compound $2BCl_3,9NH_3$, which alters but slowly when exposed to air, and does not lose ammonia below 50°, but is immediately decomposed by water with production of a slightly alkaline solution.

Berzelius obtained from ammonia and boron chloride a compound to which he gave the formula $2BCl_3,3NH_3$.

Silicon sesquichloride, Si_2Cl_6, combines directly with ammonia to form a white, solid compound, $Si_2Cl_6,10NH_3$, which does not lose ammonia below 100°, but is decomposed by water with production of a feebly alkaline solution.

Hydrogen phosphide reduces silicon sesquichloride, even at −10°, with production of the solid hydrogen phosphide. C. H. B.

Oxidising and Decolorising Properties of Charcoal. By P. CAZENEUVE (*Compt. rend.*, **110**, 788—790).—Animal or vegetable

charcoal which has been allowed to cool in contact with air exerts a distinct oxidising influence on such compounds as α-naphthylamine, paraphenylenediamine, the colouring matter of wine, &c. Its activity in this respect is comparable with that of hydrogen peroxide. This behaviour explains the well-known fact that certain solutions, such as those of phenolic compounds or of tannin matters, are not decolorised, but acquire a darker colour, when treated with animal charcoal.

It would seem that this oxidising action plays an important part in the decolorisation of liquids, the colouring matter being not only absorbed, but also oxidised. After some time, the colouring matter absorbed by animal charcoal from wine cannot be recovered by treatment with alcohol, because it has been oxidised to colourless compounds. Charcoal which has cooled in contact with carbonic anhydride has, in most cases, a distinctly lower decolorising power than charcoal which has cooled in contact with air. C. H. B.

Condensation of Carbonic Oxide under the Influence of the Silent Discharge. By P. SCHUTZENBERGER (*Compt. rend.*, **110**, 560—565).—Brodie and Berthelot observed that when carbonic oxide is subjected to the silent electric discharge, it is converted into carbonic anhydride and a brown substance, to which the former gave the formula C_4O_3, and the latter the formula C_5O_4.

The author finds that the composition of the dark-brown product is variable, and that the condensation of the carbonic oxide ceases as soon as the gas contains 10 per cent. of carbonic anhydride. The experiments were made with a simple discharge tube of the Wilde-Berthelot form, the open end dipping under mercury, whilst the armatures were acidified water. Under these conditions, the rate of condensation varied considerably, but was practically constant for the same tube used in the same way. The solid product had the composition C, 45·6; H, 0·6; O, 53·8 = 100·0. When the armatures of acidified water were replaced by mercury, condensation was much slower, and the black product had the composition C, 46·4; H, 0·9; O, 52·7 = 100·0. If the armatures were surrounded by jackets containing dry air, and every precaution was taken to exclude moisture, very little condensation took place, even when the discharge was continued for 48 hours. It follows that the presence of small quantities of water is essential to the formation of the black product, and the author is of opinion that the electric discharge carries oxygen and water through the glass, and that there is also some evidence of a transport of matter in the opposite direction, since the total quantity of carbon in the condensed product and the carbonic anhydride was less than that in the carbonic oxide which disappeared. C. H. B.

Condensation of Carbonic Oxide and the Penetrability of Glass by Water. By BERTHELOT (*Compt. rend.*, **110**, 609—612).—Condensation of carbonic oxide under the influence of the silent electric discharge takes place even when the gas is separated from water by the walls of two tubes and by an intervening air space, the gas and the apparatus having been very carefully dried. The con-

densation and the composition of the residual gas show that the solid matter has the composition C_4O_3, which confirms the author's earlier experiments. The solid product is extremely hygroscopic, and gives off water if it is heated after having been exposed to the air. If, however, it has been kept out of contact with air, no evidence can be obtained of the presence of hydrogen in it. The author concludes that there is no evidence that the discharge causes the passage of water through the glass. C. H. B.

Condensation of Carbonic Oxide. By P. SCHUTZENBERGER (*Compt. rend.*, **110**, 681—684).—Carbonic oxide was carefully dried with phosphorus pentoxide, and subjected to the action of the silent discharge in an apparatus surrounded by a jacket of dry air. Condensation took place to the extent of 20 c.c., 5 c.c. of carbonic anhydride being formed, and 15 c.c. of the carbonic oxide condensed to a black substance which contained 0·00012 gram of hydrogen, equivalent to about 0·001 gram of water. No further condensation took place, because, according to the author, the small quantity of moisture present had all been converted into the black product. If, however, the metallic armatures were replaced by armatures of acidified water, condensation recommenced, and went on continuously. The author considers this result as further proof that under the influence of the discharge the elements of water pass through the glass (compare preceding and next abstracts). C. H. B.

Observations on the Preceding Paper and on the Drying of Gases. By BERTHELOT (*Compt. rend.*, **110**, 684—685).—Glass and mercury can only be perfectly dried when heated to a moderately high temperature. If exposed to moist gases, a film of water condenses on the surface of the glass or metal, and cannot be removed at the ordinary temperature. If the mercury and the india-rubber connections of a mercurial pump are in contact with moist air, traces of water may be introduced into any apparatus which is connected with the pump. The author considers that the traces of moisture which passed into Schutzenberger's apparatus (preceding abstract) were derived from sources of this kind, and did not pass through the glass. C. H. B.

Films of Vaporised Metal. By W. N. HARTLEY (*Proc. Roy. Soc.*, **46**, 88—90).—Condensed electric sparks from an induction coil are passed between electrodes of the metals to be tested, a perforated plate of mica being interposed in the path. Rings of varying colour and diameter are produced. They are metallic in the case of the noble metals, but consist of oxides when the more oxidisable metals form the electrodes. Gold gives films of extreme tenuity, partly of a deep red or rose tint, but more frequently of a blue colour. The silver films are yellow, with a tinge of rose or violet. Silver containing $\frac{1}{100000}$th of gold gives distinct evidence of gold, and the metal, even when prepared by the processes of Stas, gives a faint indication of gold. H. K. T.

Reduction of Oxides with Magnesium. By C. WINKLER (*Ber.*, **23**, 772—792; compare this vol., pp. 331, 451).—This paper deals with the oxides of the third group of the periodic system.

When an intimate mixture of powdered boric anhydride (1 mol.) and metallic magnesium (3 atoms) is ignited, preferably in a current of hydrogen, a dark-brown mass is formed, which is attacked only with difficulty by water or alkalis, but dissolves easily and completely in hydrochloric acid or in solution of ammonium chloride, in the former case with evolution of hydrogen. It appears to be a mixture of magnesium borate (MgB_2O_4) with a boride of magnesium, Mg_9B_2. An attempt to prepare the oxide BO by heating boric anhydride (1 mol.) with magnesium (1 at.) was unsuccessful, the same reaction taking place as when 3 atoms of magnesium were used. Borax (1 mol.) was then heated with magnesium (7 at.), both substances being finely powdered and intimately mixed. The mixture became incandescent, sodium volatilised, and a dark-brown mass was obtained which evolved hydrogen slowly when treated with cold water, rapidly with hot water or hydrochloric acid. By repeatedly boiling it with water, a solution containing sodium metaborate was obtained, together with a residual black powder, probably a magnesium boride, Mg_2B_5, which was oxidisable, and dissolved in hydrochloric acid with evolution of hydrogen; this hydrogen had an unpleasant smell, and not infrequently inflamed spontaneously. The analytical data show that the following reaction, or something very like it, must have taken place:—$3Na_2B_4O_7 + 21Mg = 4Na + 2NaBO_2 + 17MgO + 2Mg_2B_5$. The black powder, when treated with strong hot hydrochloric acid until the evolution of gas has ceased, leaves a residue which resembles amorphous boron in appearance, but has been shown to be a hydride (B_8H) of that element; it is an easily oxidisable substance, and differs markedly from boron in its chemical properties. Evidence was also obtained of the formation of a gaseous boron hydride; indeed the hydrogen evolved in all the cases mentioned above had an unpleasant odour, and was probably mixed with some such gaseous compound. This compound could not be isolated, but it is probably not the normal hydride BH_3.

Aluminium oxide (alumina), 1 mol., when heated with magnesium (3 at.), glows and forms a dark-grey mass which evolves hydrogen and gradually becomes colourless when it is treated with water or hydrochloric acid. This product appears not to be a mixture of metallic aluminium and magnesium oxide, but was found to contain free magnesium and unreduced alumina; probably it contained alumina in the form of a lower oxide, AlO. To see if this was the case, alumina (1 mol.) was heated with magnesium (1 at.) in a current of hydrogen, when a nearly black powder was obtained. This was found to contain more than 40 per cent. of the oxide AlO, together with magnesia and unaltered alumina; these last two substances had combined together to some extent, forming an artificial spinel.

Yttrium oxide is quietly and seemingly completely reduced by ignition with magnesium.

Lanthanum oxide is also completely reduced; a slight incandescence is observable, but the reaction otherwise goes smoothly.

Gallium oxide is reduced by magnesium, the reaction being somewhat violent, not to say explosive, in character.

Indium oxide, when heated with magnesium, becomes incandescent, and gives rise to a violent reaction; the tube was destroyed, and the material scattered. An attempt to prepare a lower oxide, analogous to AlO, was unsuccessful.

Thallic oxide, when heated with magnesium, is decomposed by the first application of heat into oxygen and thallous oxide, and no further reduction takes place. Thallous carbonate, however, is reduced by magnesium with explosive violence, and the glass tube was shattered.

It would thus appear that, in this third group of oxides, the energy with which reduction by magnesium takes place is much greater in the second division of the group than in the first, and in each division increases with the atomic weight of the element concerned.

C. F. B.

Potassium Silicofluoride. By K. PREIS (*Listy Chem.*, **13**, 150—151).—Hexagonal crystals of this salt, which was hitherto known only in tesseral crystals, were found, together with calcium sulphate, as a deposit in a large basin containing phosphoric acid of 20° B., prepared from phosphorites in the chemical works of Pečky, Bohemia. Small, regular crystals of the same compound were found, together with the hexagonal form. The faces are 0P and 2P, and their inclination = 115° 57′, so that the axial ratio $a : c = 1 : 0{\cdot}8898$ shows its isomorphism (isodimorphism) with ammonium silicofluoride, the latter being also dimorphous. B. B.

New Form of Ammonium Chloride. By G. GEISENHEIMER and F. LETEUR (*Compt. rend.*, **110**, 576—577).—A saturated solution of ammonium chloride, which had been used for washing the precipitated double chlorides in the preparation of pure iridium by the method of Deville and Debray, deposited the salt in long, pale-rose or brown-red crystals, which contained 0·71 to 0·93 per cent. of ruthenium in the form of subchloride. On recrystallisation, the crystals became quite white. The crystals were macles; the tangents to the centres of two faces made an angle of 65° 15′, and the tangents to the faces along an edge made an angle of 82° 30′. It is probable that these crystals consist of the modification of ammonium chloride described by Le Bel (this vol., p. 475), made stable by the presence of the small quantity of ruthenium subchloride. C. H. B.

Action of Sodium Thiosulphate on Silver Salts. By J. FOGH (*Compt. rend.*, **110**, 709—711).—The decomposition of silver nitrate (2 mols.) by sodium thiosulphate (1 mol.) with formation of sodium nitrate, silver sulphide, and dissolved sulphuric acid, is complete in four or five minutes, and develops +46 Cal. at 15°. The calculated result is +45·2, but it is deduced from a large number of different experiments and data, and can only be regarded as approximate. The reaction takes place in two phases, namely, the formation of silver thiosulphate and the decomposition of the latter in presence of water, but the thermochemical disturbances corresponding with each phase could not be determined directly because of the rapidity of decomposition. Calculating from analogy, the heat of formation of silver

thiosulphate is +104 Cal., and hence the first phase of the reaction should develop +5·2 Cal., and the second +40 Cal., a result which explains the fact that the decomposition becomes complete without the aid of extraneous energy.

The dissolution of silver thiosulphate in excess of a solution of sodium thiosulphate, develops +34·8 Cal. at 12°. The conversion of silver chloride and bromide into thiosulphate would absorb 13 × 2 Cal., and 17·3 × 2 Cal., and the solution of these compounds in a solution of sodium thiosulphate is determined by the formation of the sodium silver thiosulphate. The conversion of silver iodide into thiosulphate would absorb 48·4 Cal., a quantity greater than that developed by the combination of silver thiosulphate and sodium thiosulphate, and hence a solution of sodium silver thiosulphate yields a precipitate of silver iodide on addition of a soluble iodide, and silver iodide does not dissolve in sodium thiosulphate solution without the aid of extraneous energy. C. H. B.

Monocalcium Phosphate. By I. STOKLASA (*Listy Chem.*, 13, 203—210, 240—243, 273—283).—Monocalcium phosphate, $CaH_4(PO_4)_2 + H_2O$, was prepared by dissolving pure dicalcium phosphate in 31 per cent. phosphoric acid, and recrystallising. It was then washed with absolute alcohol and ether, and dried. Washing with ether only (Erlenmeyer, Birnbaum, Wattenberg) never removes the free phosphoric acid completely, so that if prepared in this way it may contain several per cent. of free phosphoric acid. The presence of the latter may be proved, either by treatment with absolute alcohol, or by dissolving the salt completely in water and estimating volumetrically with decinormal potash in the presence of methyl-orange. Alcohol containing only small quantities of water decomposes monocalcium phosphate. The author finds that even the purest preparations decompose in closed vessels spontaneously, so that about 0·05 of free acid is formed in a month.

Monocalcium phosphate is not hygroscopic, as usually stated, especially by Birnbaum and Packard. It attracts some moisture in an atmosphere saturated with aqueous vapour, but loses it again in dry air. The hygroscopic nature of the preparation observed by the authors quoted above is, as the author shows, due to the presence of free phosphoric acid, of which at least 0·2 per cent. must have been present in Birnbaum's specimen. Steam at 80° decomposes monocalcium phosphate. With regard to the very discrepant statements as to the decomposition of monocalcium phosphate by cold water, the author has treated pure preparations with varying quantities of water, and gives his results in a tabular form; the decomposition being represented by the general formula $a CaH_4(PO_4)_2,H_2O + H_2O = (a - 1)CaH_4(PO_4)_2,H_2O + CaHPO_4 + 2H_2O + H_3PO_4$. For example, for 1 part of salt and 1 part of water $a = 4$, and, therefore, the quantity of undecomposed salt going into the aqueous solution $(a - 1) = 3$, 26 per cent. of the salt being decomposed in the above manner. With increase in the quantity of water, more salt goes into solution, and when 1 part of salt is treated with 200 parts of water, the decomposition is very small, whereas the solution is complete; here

$a = 1024$, and from this only 1 part is decomposed = 0·1 per cent. The decomposition is regular, for, whereas, for the proportion of 1 salt : 1 water, the quantity of free phosphoric acid formed = 7·51, for 1 salt : 25 water, that quantity becomes one-half this = 3·75, and for every increase of 25 parts of water again one-half of the previous amount. The salt dissolves in 200 parts of water to a clear solution, and at this point it becomes impossible to prove the existence of the free acid, which would indicate decomposition. Above this limit the monocalcium phosphate is re-formed from its products of decomposition—dicalcium phosphate and phosphoric acid.*

Free phosphoric acid, added to monocalcium phosphate solutions, prevents their decomposition. If we add to monocalcium phosphate such a quantity of free phosphoric acid as would be formed by the decomposition of the salt, no decomposition takes place; for example, for 1 salt : 1 water, this quantity will be 7·5 per cent., as seen from the result stated above. If Erlenmeyer finds the solubility of the salt 1 : 100, it follows that the presence of 0·4 per cent. of free phosphoric acid in his salt had prevented the decomposition and increased the solubility.

The author's conclusions as regards the solubility of superphosphates and disuperphosphates in water, are of technical interest.

B. B.

Strontium Chlorate and the Velocity of its Decomposition by Heat. By A. Potilitzin (*J. Russ. Chem. Soc.*, **21**, 451—466; compare Abstr., 1888, 219; 1889, 338; this vol., p. 333).—Strontium chlorate, according to Wächter (*J. pr. Chem.*, 1843, **30**, 231) and Topsöe, is anhydrous; according to Louchay, it crystallises with 5 mols. H_2O. It is always described as very deliquescent. The author prepared the salt by repeated recrystallisation of the commercial preparation, until its solution gave no precipitate with silver nitrate. At the ordinary temperature, the salt crystallises in transparent, rhombic octahedra, which are almost insoluble in absolute alcohol, and not deliquescent. It attracts some moisture in wet weather, and loses it again in dry weather; if, however, the salt contains strontium chloride, it is deliquescent. It forms supersaturated solutions, and, according to the author's theory, it ought to exist in allotropic modifications (this vol., p. 333); this was found to be the case. On gradually cooling its hot saturated solution to 10°, small, monoclinic scales are obtained, but after a time the ordinary octahedral crystals are deposited from the same solution. A third form of this salt is obtained at the ordinary temperature from a very strong supersaturated solution, but only when the liquid has a certain concentration; it forms long prisms or scales, but if these are left in the mother liquor, from which they have separated, they soon dissolve again. A fourth form of the salt separates from a solution of the salt at 70—90°; these crystals are long, rhombic prisms, but only a small quantity was obtained. The hydrated salt, $Sr(ClO_3)_2 + 3H_2O$, was prepared by taking a 59 per

* Probably a state of unstable equilibrium sets in between these three substances, if Mendeléeff's theory of solution is correct.—B. B.

cent. solution of the salt, and cooling it to $-40°$; fine, needle-shaped crystals then separated, together with some ice, and on placing these in another solution containing 64 per cent. of the salt, cooled to $-20°$ or $-25°$, they continued to grow, and then formed four-sided prisms with a pyramidal end, belonging to the rhombic system; these lose their water completely, when exposed to the air at the ordinary temperature. A solution of the salt containing 64 per cent., when cooled in a closed vessel, to $-95°$, is gradually converted into a gelatinous mass, and no change is brought about by the introduction of a crystal of the anhydrous or of the hydrated salt, but when the solution becomes mobile at $-70°$ to $-60°$, a crystal of the hydrated salt grows slowly, and crystals of the trihydrated salt are formed in the liquid. The composition of the above gelatinous mass, formed at $-95°$, corresponds with the formula $Sr(ClO_3)_2 + 8H_2O$.

On heating the anhydrous salt, a very slow decomposition ensues at 290°. When, at a higher temperature, 10 per cent. of oxygen has been given off, the salt fuses, and then consists of a mixture of $Sr(ClO_3)_2 + Sr(ClO_4)_2 + SrCl_2$. The rate of decomposition of the chlorate is somewhat rapid at first, up to the point when the salt begins to fuse; then the decomposition becomes slower. When the loss amounts to 10 per cent., it fuses completely, and the rate of decomposition again increases up to a loss of 16 to 20 per cent. at 368°, after which the rate of decomposition is found to diminish; the loss amounting to 28—29 per cent. after heating for 30 minutes at 395°. The total decomposition (a loss of 37·7 per cent.) is reached only after 19 hours 35 minutes. The decomposition of strontium chlorate, in its different phases, is represented by the general formula $ASr(ClO_3)_2 = mSrCl_2 + nSr(ClO_4)_2 + pO$. Different samples of the chlorate were heated for different intervals of time up to a temperature of 368°, and the products of reaction were again weighed and analysed in the same manner as in the case of lithium chlorate. A small quantity of strontium oxide was formed at the same time. As long as any excess of chlorate is present, the reaction tends to produce a maximum of perchlorate, and this maximum is reached when about three-fourths of the chlorate is decomposed. In this phase the decomposition is represented by the following reaction:—

$$11Sr(ClO_3)_2 = 9SrCl_2 + 2Sr(ClO_4)_2 + 25O_2.$$

Later on the quantity of perchlorate diminishes, and when 25 per cent. of oxygen has been evolved, the relation becomes $7Sr(ClO_3)_2 = 6SrCl_2 + Sr(ClO_4)_2 + 17O_2$. That strontium perchlorate is decomposed according to the equation $ASr(ClO_4)_2 = nSrCl_2 + mSr(ClO_3)_2 + pO_2$, has been shown by direct experiments, which will form the object of a future communication. B. B.

Beryllium. By G. Krüss and H. Moraht (*Ber.*, **23**, 727—737).—The material employed in this investigation was a light-green leucophane from Arendal, in Norway. In order to isolate the beryllium oxide, the mineral, separated as far as possible from the tourmaline contained in it, was finely powdered, mixed with water to form a

paste, and an excess of concentrated sulphuric acid added. After evaporating off most of the acid, the above treatment was repeated, and the residue extracted with water, the extract poured into an excess of ammonium carbonate solution, and an excess of ammonia added. After remaining for 10 days, the precipitate was filtered off, the filtrate boiled, and the precipitate then formed was collected, washed, and ignited. The residue consists chiefly of beryllium oxide, mixed with ferric oxide and alumina. The last two compounds are, as A. Zimmerman has pointed out (*J. pr. Chem.*, **76**, 1), extremely difficult to remove, and in the further purification his method was adopted. The mixture of oxides was dissolved in hydrochloric acid, precipitated with ammonia, and a quantity of ammonium carbonate solution added, which was insufficient to dissolve the whole of the precipitate. After 10 days the solution was filtered, and, as suggested by Humpidge (*Proc. Roy. Soc.*, **39**, 1), a strong current of steam passed through the solution, and the first portion of the precipitate taken, and subjected to the same treatment four times. The precipitate of beryllium oxide finally obtained was free from iron and snow-white.

The reduction of the oxide by means of magnesium powder (this vol., p. 451) gave a metal contaminated with silica. To obtain a purer beryllium, the oxide was converted into potassium beryllium fluoride, H_2BeF_4, by dissolving the oxide in hydrofluoric acid, adding potassium fluoride to the concentrated solution, and recrystallising the salt repeatedly from water. This was heated to bright redness for 31 minutes with the calculated quantity of sodium in a steel crucible. In the residue, hexagonal crystals of beryllium could be seen, as well as beryllium powder, slightly contaminated with iron and beryllium oxide. In a second experiment, the mixture was heated at a lower red heat for 26 minutes; the beryllium thus obtained was free from iron, but contained a considerable quantity of beryllium oxide.

Beryllium oxide behaves as a feeble acid towards strong bases. *Potassium beryllate*, $Be(OK)_2$, obtained by dissolving beryllium oxide in aqueous or alcoholic potash, forms a snow-white mass with a silky lustre, but cannot be obtained free from potassium carbonate.

Towards feeble acids beryllium oxide behaves as a base. Aqueous sulphurous acid dissolves freshly precipitated beryllium hydroxide, and the solution, on evaporation, leaves a gummy mass, of the composition $BeSO_3,BeO$. If this be treated with alcohol and a little sulphurous acid, and the solution again allowed to evaporate, a second amorphous basic sulphite, $3BeSO_3,BeO$, is obtained. If, however, the freshly precipitated hydroxide be added to a saturated alcoholic solution of sulphurous anhydride, the solution gives a white, crystalline residue on evaporation in a vacuum over sulphuric acid and alkali. Its analysis shows it to be the normal sulphite $BeSO_3$, but it is decomposed by both alcohol and water.

Freshly precipitated beryllium hydroxide does not act on boric acid, and barium borate gives no beryllium borate on treatment with beryllium sulphate, but simply the hydroxide. The borate may, however, be obtained by precipitating beryllium chloride solution with borax

solution, or by neutralising the same with sodium carbonate in presence of a large excess of boric acid. It is a white precipitate, resembling beryllium hydroxide, and has the composition $5BeO,B_2O_3$.

The beryllium oxide obtained by the method above described dissolves in concentrated hydrochloric acid with a greenish-yellow colour. This fact, although not previously published, has, according to private communications to the authors, also been observed by Joy, Nilson, and Petterson, and is due to the presence of some impurity, which may be removed as follows:—The colourless solution obtained after the purification with ammonium carbonate is treated with ammonium sulphide, thoroughly shaken, allowed to remain for two days in a well-closed bottle, and filtered from a small quantity of black precipitate formed. The beryllium carbonate obtained on boiling the filtrate and the beryllium oxide formed from the latter by ignition, then dissolve in concentrated hydrochloric acid with formation of a perfectly colourless solution.

The beryllium oxide thus purified was utilised for a redetermination of the atomic weight of beryllium. The numbers obtained varied from 9·08 to 9·25, the lower number being that previously obtained by Nilson and Petterson. H. G. C.

Lead Tetrachloride. By I. FRIEDRICH (*Listy Chem.*, **17**, 67—68).—In this preliminary notice the author refers to the work of Nikoljukin (*J. Russ. Chem. Soc.*, 1885, 207—210), who prepared the double salts of ammonium chloride and of potassium chloride with lead tetrachloride without entering more fully into the subject. The very stable ammonium double salt yielded, by a method which the author proposes to describe more fully, a liquid of 3·2 sp. gr., which above 0° is decomposed into lead dichloride and free chlorine; the analysis of this compound shows that it is lead tetrachloride, $PbCl_4$.

B. B.

Lead Oxides. By G. KASSNER (*Arch. Pharm.* [3], **28**, 171—178).—The author briefly discusses views which have been published on the composition of the various oxides of lead. In a previous paper (this vol., p. 561) he has described the production of plumbates corresponding with the ortho-acid H_4PbO_4, which has not yet been isolated. The already known hydrate PbO_2,H_2O, obtained as a bluish-black deposit at the positive pole when lead solutions are decomposed by the electric current, may be represented by $PbO(OH)_2$, and as it contains a molecule less water than the ortho-acid, may be called metaplumbic acid; lead sesquioxide may be expresed as a salt of this acid, $PbO{:}O_2{:}Pb$. The oxide Pb_3O_4 follows as an orthoplumbate, $Pb(O_2Pb)_2$. The peroxide, PbO_2, is to be considered as the anhydride both of orthoplumbic and metaplumbic acid. Other compounds of lead and oxygen are known besides the ortho- and meta-plumbates, such compounds as Pb_4O_5, Pb_5O_7, &c. These compounds cannot be considered as simple molecular aggregates of PbO and Pb_3O_4, but must be chemical compounds, seeing that they resist the action of weak solvents which would otherwise take up PbO. Structural formulæ which may represent Pb_4O_5 are given. The composition of the earthy plumbates indicates that only tetratomic lead is present.

Genther has shown that lead oxide does not contain PbO, but a polymeride of this, either Pb_3O_3 or Pb_6O_6; consequently in the formation of the plumbates this polymeric molecule must undergo decomposition; it is, therefore, probable that the polymeric molecule only exists as such in the cold, whilst molten lead oxide consists of the simple molecule PbO. J. T.

Lead Thiosulphate. By J. FOGH (*Compt. rend.*, **110**, 522—523).—When dilute solutions of lead acetate and sodium thiosulphate are mixed, the lead is completely precipitated in the form of anhydrous thiosulphate, PbS_2O_3, with development of +5·8 Cal. at 10°. This corresponds with +8·6 Cal. for the solid acetate and thiosulphate. The lead thiosulphate immediately after precipitation dissolves completely in a solution of sodium thiosulphate with absorption of −0·392 Cal. at 11°. The dried precipitate requires a stronger solution of the sodium salt for rapid solution, but the absorption of heat (−0·418 Cal.) is practically the same, and hence the physical condition of the thiosulphate is not changed during the process of washing and drying. It follows that as the heats of formation of lead acetate and sodium acetate and thiosulphate from their elements are known, the heat of formation of the lead thiosulphate from its elements can be calculated from the result of the first experiment. Taking the heat of formation of dissolved thiosulphuric acid as +79·4 Cal.,

$$Pb + S_2 + O_3 = Pb_2S_2O_3\text{, develops } +152 \text{ Cal.}$$

C. H. B.

Decomposition of Lead Thiosulphate by Heat: Lead Trithionate. By J. FOGH (*Compt. rend.*, **110**, 524—525).—When dry lead thiosulphate is heated, it yields lead sulphide, lead sulphite, lead sulphate, and sulphurous anhydride; but if the thiosulphate is boiled with water for a long time, the sole products are lead sulphide and lead trithionate in equal molecular proportions.

Lead trithionate also separates very slowly in small, slender needles from a mixture of saturated solutions of lead acetate and potassium trithionate. When dried in a vacuum, it is anhydrous. If heated gently, sulphur is given off; and if heated more strongly, sulphur vapour and sulphurous anhydride are evolved, and a black residue is left. It is only slightly soluble in water, and the solution may be boiled for some time without alteration, but if evaporated on a water-bath, partial decomposition into sulphide and sulphate takes place.

Lead trithionate dissolves completely in a solution of sodium thiosulphate; heat of dissolution = − 5·0 Cal. at 10°—

$Pb + S_3 + O_6 + Aq = PbS_3O_6$ diss. ..	develops	+280·2 Cal.
$Pb + S_3 + O_6 = PbS_3O_6$ solid	,,	+285·2 ,,

The conversion of lead thiosulphate into the sulphide and the trithionate is endothermic and, if the trithionate is all dissolved, is accompanied by an absorption of about −6·0 Cal. C. H. B.

Lead Sodium Thiosulphates. By J. FOGH (*Compt. rend.*, **110**, 571—573).—Lead sodium thiosulphate is obtained by mixing solu-

tions of sodium thiosulphate and lead acetate, and adding alcohol to the mixture. If the solutions are concentrated, the liquid separates into two layers, and when the lower layer is treated with more alcohol, it solidifies to a white, amorphous mass of variable composition. The heat of solution of this product indicates that it is a mixture of lead sodium thiosulphate and hydrated sodium thiosulphate, and it is probable that the complex lead sodium thiosulphates described by previous investigators were really mixtures of the same kind.

If the solutions are dilute, a white, gelatinous precipitate forms and gradually changes to crystalline plates. When dried in a vacuum, the crystals have the composition $PbS_2O_3,2Na_2S_2O_3$, and are identical with the double salt described by A. Lenz. The heat of solution of this compound in a dilute solution of sodium thiosulphate is $-4·1$ Cal. at 10°, and hence its heat of formation from its constituent salts is $+5·3$ Cal. C. H. B.

Conditions of the Reaction between Copper and Nitric Acid. By V. H. VELEY (*Proc. Roy. Soc.*, **46**, 216—222).—Spheres of copper, introduced into dilute nitric acid and kept in violent agitation (compare Trans., 1889, 361), were found to be more rapidly attacked by acid which had been previously used in similar experiments than by fresh acid. The increased rate of solution was found to be due to the nitrous acid generated. Nitric acid of sp. gr. 1·41 was freed from nitrous acid by passing a current of air through it at at a temperature not exceeding 30°. When the copper spheres were introduced into this acid, no evolution of gas occurred for three minutes, but the acid contained a considerable quantity of nitrous acid after five minutes. If carbamide be added to the acid, the action is considerably retarded, but proceeds rapidly when once commenced. In one experiment in which 1 gram of carbamide was added to a litre of the acid, the copper sphere remained unattacked during a period of an hour. A current of air driven through the acid has the same effect as carbamide in removing nitrous acid and preventing the solution of the copper. H. K. T.

Action of Sulphuric Acid on Aluminium. By A. DITTE (*Compt. rend.*, **110**, 573—576).—When aluminium foil is placed in sulphuric acid of 2·5 per cent., it at first seems to undergo no change, but after a time the surface loses its polish and becomes matt, and bubbles of gas appear and increase in quantity as the surface becomes rougher. Eventually the aluminium dissolves completely. In a vacuum, the phenomena are similar, but follow one another more rapidly, the air condensed on the surface being given off first, followed as soon as the pressure is low by the hydrogen liberated by the action of the acid. Like amalgamated zinc, the aluminium is attacked immediately on its immersion in the acid, but the surface becomes covered with a film of hydrogen, which prevents further action.

If the sulphuric acid is mixed with a small quantity of any chloride with a heat of formation greater than that of aluminium chloride (platinum, gold, copper, mercury), the evolution of hydrogen is much more rapid. The chlorides of iron, zinc, &c., have no such effect.

In presence of traces of the active chlorides, the evolution of hydrogen is at first rapid, but after a time it slackens, and a white deposit of basic aluminium sulphate, $2Al_2O_3,SO_3$, is formed, and increases in quantity until the whole of the aluminium has been dissolved.

Aluminium, under atmospheric pressure, is not attacked by a solution of aluminium sulphate, but in a vacuum, air is first disengaged from the surface of the metal, and the latter is then converted into the basic sulphate with evolution of hydrogen. The same change takes place readily even under atmospheric pressure if a trace of one of the active chlorides is added.

The displacement of copper from copper sulphate by aluminium is an exothermic change, but does not take place under ordinary conditions even in presence of free acid. After prolonged contact, the aluminium is slowly attacked, the rapidity of the reaction increasing as the surface of the metal becomes roughened. In presence of a trace of one of the active chlorides, the deposition of copper is much more rapid, even in absence of free sulphuric acid.

The same explanation holds in all cases where the aluminium does not readily enter into a reaction which would be exothermic. The surface of the metal becomes covered with a thin layer of gas, which prevents further change, but which can be removed by reduction of pressure or by the roughening of the surface of the aluminium in consequence of the deposition of another metal upon it. C. H. B.

Action of Nitric Acid on Aluminium. By A. DITTE (*Compt. rend.*, **110**, 782—784).—The action of nitric acid and nitrates on aluminium, like the action of sulphuric acid and sulphates (preceding abstract), is impeded by the formation of a film of gas on the surface of the metal. If the action takes place in a vacuum, or if the liquids are heated, dissolution of the metal takes place much more rapidly. Very dilute nitric acid yields nitrogen, nitric oxide, and ammonia. Nitric acid of 3 per cent., mixed with a small quantity of platinum chloride, dissolves aluminium with very slight evolution of gas and formation of considerable quantities of ammonium nitrate. Aluminium dissolves in a solution of the normal nitrate, especially on heating, with evolution of hydrogen and formation of the basic nitrate $2Al_2O_3,N_2O_5,10H_2O$. At the ordinary temperature, dissolution takes place very slowly, but the action is somewhat more rapid in a vacuum. The decomposition of water by aluminium would result in the formation of the hydroxide and hydrogen, either of which can form a protecting film on the surface of the metal. In presence of any salt which will dissolve the aluminium hydroxide, the metal is gradually attacked. Salts which do not dissolve alumina have no influence on the change. C. H. B.

Fluoroxy-salts of Molybdenum. By F. MAURO (*Gazzetta*, **19**, 179—195).—After an historical account of the molybdenum compounds of the type MoX_5, the author calls attention to the fact that the pentachloride and the compound $MoCl_5,POCl_3$ are the only compounds of that class the composition of which is firmly established, inasmuch as Blomstrand's analyses of his violet and brown oxychlorides

(*J. pr. Chem.*, **71**, 459) do not agree sufficiently well with the formulæ calculated, whilst the generally received formula for the blue oxide, Mo_2O_5, depends on the analyses of Wöhler and Buff (*Annalen*, **110**, 275), and of Rammelsberg (*Ann. Phys. Chem.*, **127**, 290), all of which agree better with the formula Mo_3O_8. Rammelsberg's analyses of the hydrated oxide $Mo_2O_5,3H_2O$ likewise agree better with the formula $Mo_3O_8,5H_2O$.

Normal potassium fluoroxyhypomolybdate, $MoOF_3,2KF,H_2O$, is best obtained by adding potassium hydrogen fluoride to a solution of hydrated molybdenum dioxide in hot hydrofluoric acid; on cooling, the hypomolybdate separates in very thin, blue plates. It may also be prepared by the electrolysis of a solution of potassium fluoroxymolybdate, $MoO_2F_2,2KF,H_2O$, in dilute hydrofluoric acid. It crystallises from a solution containing excess of hydrofluoric acid in large, transparent, monoclinic laminæ, having a vitreous lustre—

$$a : b : c = 0{\cdot}99975 : 1 : 1{\cdot}03200;\ \beta = 80^\circ\ 56'\ 27''.$$

Forms observed—(100), (010), (001), $(10\bar{1})$, (021), (111), (110), $(11\bar{1})$, $(11\bar{2})$.

Principal angles $001 : 100 = 80^\circ\ 56'$; $001 : 10\bar{1} = 129^\circ\ 24'$; $001 : 021 = 63^\circ\ 52'$; $001 : 111 = 51^\circ\ 7'$; $001 : 110 = 83^\circ\ 34'$; $001 : 11\bar{1} = 120^\circ\ 9'$; $110 : 1\bar{1}0 = 89^\circ\ 16'$.

From these figures it appears that potassium fluoroxyhypomolybdate may be regarded as geometrically isomorphous with the salts $MoO_2F_2,2KF,H_2O$; $WO_2F_2,2KF,H_2O$; $NbOF_3,2KF,H_2O$; and $TiF_4,2KF,H_2O$.

It acquires a more intense blue colour after prolonged exposure to the air, but it undergoes no further change. It loses the greater part of its water of crystallisation when placed in dry air over calcium chloride, and it turns green and becomes anhydrous on heating at 100°. When ignited for several hours in the air, it loses hydrofluoric acid, and is converted into normal potassium molybdate. It is soluble in water and in hydrochloric acid with decomposition, and like other substances of this class it is a powerful reducing agent, precipitating salts of silver, copper, gold, &c.

Hexagonal potassium fluoroxyhypomolybdate, $3MoOF_3,5KF,H_2O$, is obtained by dissolving the preceding salt in hydrofluoric acid and concentrating the solution; on cooling, the hypomolybdate separates out in very slender blue, vitreous, acicular crystals, which appear under the microscope as prisms with a hexagonal section. It is soluble in water with decomposition, and has considerable reducing power; it gives off hydrofluoric acid on heating to 230°.

Normal ammonium fluoroxyhypomolybdate, $MoOF_3,2NH_4F$, is obtained by gradually adding ammonia to a solution of the hydrated molybdenum dioxide in hydrofluoric acid until the dark-green colour changes to brownish-red; more hydrofluoric acid is then added, until the original colour is just restored. On concentrating the solution at a moderate temperature, the ammonium salt separates out in large blue or green, vitreous, transparent, rhombic prisms or tables, which become deep blue on exposure to the air—

$$a : b : c = 0{\cdot}84289 : 1 : 1{\cdot}01998.$$

Forms observed :—(010), (001), (011), (034), (012), (201), (605), (101), (221).

Principal angles :—001 : 011 = 45° 34′; 001 : 034 = 37° 25′; 001 : 012 = 27° 01′; 001 : 201 = 67° 33′; 001 : 605 = 55° 27′; 001 : 101 = 50° 26′; 001 : 221 = 72° 28′; 221 : 22$\bar{1}$ = 35° 04′; 201 : 20$\bar{1}$ = 44° 54′; 201 : 011 = 74° 30′; 011 : 221 = 49° 29′.

This salt is, therefore, isomorphous with the compounds—

$$MoO_2F_2,2NH_4F, \quad NbOF_3,2NH_4F, \quad \text{and} \quad WO_2F_2,2NH_4F.$$

From the isomorphism of the compounds $MoOF_3,2KF,H_2O$ with $MoO_2F_2,2KF,H_2O$, and of $MoOF_3,2NH_4F$ with $MoO_2F_2,2NH_4F$, it would appear that the substitution of an atom of fluorine for an atom of oxygen does not affect the crystalline form of the compound.

Hexagonal ammonium fluoroxyhypomolybdate, $3MoOF_3,5NH_4F,H_2O$, is obtained by concentrating a solution of the normal salt in hot hydrofluoric acid. On cooling, it separates out in very small, sky-blue, vitreous, acicular crystals, which appear under the microscope as hexagonal prisms with their principal axis coincident with the direction of optic extinction; in this respect it resembles the compounds $3MoOF_3,5KF,H_2O$, $3NbOF_3,5KF,H_2O$, and $3NbOF_3,5NH_4F,H_2O$. It has some reducing power and is decomposed by water; on exposure to the air, its colour changes to a deep blue.

Other ammonium fluormolybdates prepared by the author have been already described (see Abstr., 1889, 106). S. B. A. A.

Phosphotrimetatungstic Acid and its Salts. By E. PÉCHARD (*Compt. rend.*, **110**, 754—757).—*Phosphotrimetatungstic acid*,

$$P_2O_5,12WO_3 + 42H_2O,$$

is obtained by evaporating below 100° a mixture of phosphoric and metatungstic acids in any proportions whatever. If the metatungstic acid is in excess, the final crystals consist of phosphopentametatungstic acid. Phosphotrimetatungstic acid forms brilliant crystals, seemingly triclinic, which do not effloresce and are soluble in water or alcohol. They are not decomposed by acids in the cold, but tungstic acid separates on heating. With bases, the acid yields salts of the general type $M'_2O,P_2O_5,12WO_3$, which can also be obtained by the direct combination of metatungstic acid and phosphates. Excess of an alkali yields a mixture of a normal tungstate and normal phosphate. The sodium salt crystallises with 18 mols. H_2O in fine crystals, isomorphous with the acid; it is insoluble in alcohol. The potassium salt,

$$K_2O,P_2O_5,12WO_3 + 9H_2O,$$

is amorphous, insoluble in cold water, and only slightly soluble in hot water; the ammonium, cæsium, and rubidium salts have similar properties. The thallium salt, $Tl_2O,P_2O_5,12WO_3 + 4H_2O$, is a very finely divided, amorphous substance. The lithium salt, which conforms to the general type, and crystallises with 21 mols. H_2O, forms brilliant crystals, apparently rhombohedric. The barium, strontium, and calcium salts crystallise in rhombohedral crystals with 15, 17, and 19

mols. H_2O respectively, dissolve in water, but are insoluble in alcohol. The magnesium, cadmium, and zinc salts form rhombohedral crystals with 10, 13, and 7 mols. H_2O respectively. The copper salt (11 mols. H_2O) is also rhombohedral, but effloresces very rapidly; the lead salt (6 mols. H_2O) is white, and insoluble in cold water, but crystallises from boiling water in slender needles. The silver salt, $Ag_2O,P_2O_5,12WO_3 + 8H_2O$, is insoluble, and is not affected by light. The mercurous salt is yellowish, and is insoluble in water and dilute nitric acid. C. H. B.

Atomic Weight of Zirconium. By G. H. Bailey (*Proc. Roy. Soc.*, **46**, 74—87).—In this paper, experiments with a view to the preparation of pure zirconia, prior to the determination of the atomic weight of zirconium, are described. Crude zirconia was dissolved in hydrochloric acid, and crystallised out as oxychloride. A solution of the latter was treated with hydrogen sulphide, filtered, the filtrate rendered alkaline with ammonia, and any further precipitate of sulphides removed. The filtrate was then acidified, and oxalic acid added to throw down gadolinium earths. The oxychloride still contained iron, which was removed by repeated crystallisations from concentrated hydrochloric acid, the crystals being finally washed with a mixture of the acid with 1 part of alcohol and 10 parts of ether. The zirconia now contained only soda, which was removed by repeated precipitation with ammonia and re-solution with hydrochloric acid.

The following forms of zirconium were examined—the metal, the chloride, oxychloride, bromide, and sulphate. The only method which gives the metal free from foreign impurity is Phipson's, in which zirconia is heated with magnesium powder. The black powder so obtained consists mainly of zirconia, and contains only a small amount of metallic zirconium. Nearly pure metal can be obtained by using magnesium foil, the foil being afterwards treated with hydrochloric acid. The author finds that concentrated sulphuric acid acts rapidly on zirconium in the cold.

The peroxide can be precipitated in acid or ammoniacal solution, preferably the former, by means of hydrogen peroxide. It has the composition $ZrO_3,3H_2O$ when dried over phosphoric anhydride. At 100° its composition becomes Zr_2O_5.

Zirconium tetrachloride was prepared in the nsual way, and was sublimed in a current of chlorine through a tube drawn out into bulbs, a lower temperature being used for each bulb. The bulbs were then sealed aud their contents analysed. The results were not concordant.

Zirconium oxychloride is apt to retain hydrochloric acid, and if heated it passes into basic salts. Samples were purified (1) by washing with alcohol and ether, (2) by placing in a vacuum over solid potash. The ratio of chlorine to zirconium oxide was determined, and the results compared with one another and with those of Berzelius. They were not concordant.

The sulphate was prepared by heating the powdered zirconia with sulphuric acid, the excess of acid being driven off at a temperature of 350—400°, it being found that the excess of acid was completely

expelled at 350°, whilst the salt was decomposed only at temperatures above 400°.

Atomic weight of zirconium.—The decomposition of zirconium sulphate was considered to be the most accurate method for the determination of this value. Owing to the rapidity of the decomposition loss is apt to occur. The crucible in which the decomposition was effected was therefore enclosed in a second one, and heated very slowly. The mean of eight determinations gives 90·401 as the atomic weight of zirconium (H = 1). H. K. T.

Vanadium in Potassium Hydroxide. By E. F. SMITH (*Chem. News*, **61**, 20—21).—By treating ordinary stick potash with hydrogen sulphide, acidifying with hydrochloric acid, &c., as much as 0·5 gram of impure vanadium sulphide was obtained from 3 lbs. of potash.

D. A. L.

Atomic Weight of Bismuth. By A CLASSEN (*Ber.*, **23**, 938—953).—The purest commercial bismuth contains various impurities, such as copper and iron, but the principal one is lead; the author's first attempts to prepare the metal in a chemically pure condition were carried out as follows:—(1) The purest commercial metal (250 grams) was dissolved in nitric acid, the solution repeatedly evaporated with concentrated hydrochloric acid until free from nitric acid, the chloride dissolved in concentrated hydrochloric acid, and the solution mixed with alcohol, whereon the lead was partially precipitated as chloride. The filtered solution was then placed in 10 beakers (each of 4 litres capacity), the bismuth precipitated as oxychloride by adding water, the precipitate washed by decantation until free from hydrochloric acid, redissolved in hydrochloric acid, and reprecipitated with water; this process was repeated 12 times. The oxychloride obtained in this way was dissolved in hydrochloric acid, the diluted solution treated with ammonia and ammonium carbonate, the precipitate washed by decantation until free from ammonia, dissolved in hydrochloric acid and reprecipitated with ammonia and ammonium carbonate; this process was twice repeated. The precipitate was then dissolved in hydrochloric acid, reprecipitated with water, washed, dried, and fused with 98 per cent. potassium cyanide; the resulting metal was then repeatedly melted with potassium cyanide, the whole melt finally cast into a mould, and when cold, the metal separated, washed well with water, and polished.

(2.) The purest commercial bismuth nitate was treated as described in the first process.

The metal purified by either of these methods was found, on spectroscopic examination, to contain lead, so that bismuth cannot be freed from this metal by fractional precipitation.

Chemically pure bismuth can, however, be obtained by electrolysis. When a nitric acid solution of the metal, purified as described above, is electrolysed under suitable conditions, chemically pure bismuth is deposited on the negative electrode, and the whole of the lead is deposited as peroxide, together with bismuth peroxide, on the positive electrode. The electrolysis is carried out in the following manner:—About 200 grams of the purified metal is dissolved in pure

nitric acid, and the cold solution placed in a beaker; a platinum basin, resting on the bottom of the beaker and connected with a positive electrode of the usual form, serves as the positive, and a platinum cone as the negative, electrode. The current can be obtained either from galvanic batteries or from a dynamo, and is so regulated by means of resistance coils, that the bismuth separates in a crystalline condition. The bismuth and lead peroxides are deposited together on the platinum basin, and the negative electrode together with the adherent bismuth can be easily removed without agitating the liquid. The bismuth is separated from the electrode, washed with alcohol, melted with potassium cyanide as described under (1), and polished.

In this way it is obtained in a perfectly pure condition, as is shown not only by spectroscopic examination, but also by measurements of its electrical resistance (compare v. Aubel, Abstr., 1889, 807), which is the best test of absolute purity.

The specific heat of the pure metal was found by v. Aubel to be 0·0318 between 61·6° and 21·7°, as the average of 10 determinations by Kopp's method.

The specific gravity of the pure metal was determined by the author and found to be 9·7474, as the average of four experiments, and the specific gravity of pure melted bismuth oxide 9·0444.

Pure bismuth that has cooled slowly melts at 264°, but traces of impurities raise its melting point considerably.

After discussing the methods employed by previous investigators (Lagerhjelm, Schneider, Dumas, Marignac, Bailey, and Löwe), the author gives a brief account of his own preliminary attempts to determine the atomic weight of bismuth (1) by converting the metal into oxide, (2) by converting the metal or oxide into sulphide, (3) by converting bismuth triphenyl into oxide, and (4) by converting bismuth triphenyldibromide into oxide, but none of these methods gave satisfactory results.

The following method was finally adopted, and found to be both simple and accurate:—The pure metal is placed in a platinum basin (90 mm. in diameter), standing in a larger platinum basin (120 mm. in diameter), and covered with a third platinum basin (92 mm. in diameter), over which is inverted a fourth platinum basin (105 mm. in diameter), in such a way that it rests on the bottom of the largest basin; dilute nitric acid, most carefully purified, is then added, and the whole apparatus heated in the water-bath until solution is complete. The platinum basins which serve as covers are washed with dilute nitric acid, the washings added to the bismuth solution, the whole evaporated to dryness, and the residue heated first to 90—100° in an air-bath, and then, after keeping 24 to 48 hours, gradually to 250°, at which temperature the nitrate is gradually decomposed; the residual oxide is then heated to its fusing point until its weight becomes constant.

The average of nine determinations gave 208·923 (O = 16) or 208·401 (O = 15·96) as the atomic weight of bismuth, or when reduced to a vacuum 208·90235 and 208·38009 respectively, the values given above for the sp. gr. of the metal and its oxide being taken.

F. S. K.

New Bismuth Potassium Iodide. By L. ASTRE (*Compt. rend.*, **110**, 525—527).—With a view to prepare Nicklè's salt, $BI_3,KI + 2H_2O$, 38·1 grams of iodine, 14·82 grams of potassium chloride, and 100 grams of water were allowed to remain in contact with 40 grams of powdered bismuth for about two months. At the end of this time, the product consisted of slender, brown needles mixed with potassium chloride and the excess of bismuth, with a small quantity of bismuth potassium chloride. The only solvent which will dissolve the double iodide without decomposition is ethyl acetate. By spontaneous evaporation of this solvent, crystals are obtained which always have the same composition and are similar in appearance to the crystals in the crude product. The percentage composition of the crystals is as follows:—

	I.	Bi.	K.	H_2O.
Found (mean of three preparations)	64·8	32·6	2·5	—
Calc. for $KI,2BiI_3$	65·4	32·5	2·1	—
Calc. for $KI,BiI_3 + 2H_2O$	65·4	27·08	5·03	2·49

The product is therefore a double iodide, different from Nicklè's salt. It is obtained more rapidly by heating the preceding mixture at 100° in a well-closed flask for 24 hours, cooling and extracting with ethyl acetate. C. H. B.

Atomic Weight of Gold. By J. W. MALLET (*Proc. Roy. Soc.*, **46**, 71—73).—Five methods were used in this determination:—(1.) A neutral solution of auric chloride was divided into two accurately weighed portions. In one the gold was precipitated with sulphurous anhydride and weighed. With the other, the amount of metallic silver, in the form of nitrate, required to precipitate its chlorine was determined (five experiments). (2.) A similar method was applied to a solution of auric bromide (six experiments). (3.) A similar treatment was applied to a solution of potassic aurobromide (four experiments). (4.) A determination was made of the loss by ignition of a weighed quantity of trimethylammonium aurochloride (five experiments). (5.) A comparison was made of the weights of gold and silver simultaneously deposited by the same current from solutions of aurocyanide and argentocyanide of potassium respectively (five experiments). (6.) A comparison was made of the weight of gold deposited from potassium aurocyanide with the volume of hydrogen liberated from dilute sulphuric acid by the same current (three experiments). (7.) A determination was made of the quantity of hydrogen obtainable by the dissolution of zinc in dilute sulphuric acid. A definite quantity of this zinc, taken in excess, was used to precipitate gold from a neutral solution of auric chloride and the gold thrown down was determined. The excess of zinc was dissolved in sulphuric acid and the volume of the evolved hydrogen was noted. From these data the hydrogen equivalent to the precipitated gold was calculated (six experiments).

The general mean of the results is 196·910. If methods 5 and 6, which are the least satisfactory, are excluded, the value 196·882 is

obtained. Finally, if the mean of the first three methods is taken, the value 196·762 is obtained, a result higher than that of Krüss, but lower than that of Thorpe and Laurie. H. K. T.

Potassium Nitrosoplatinochloride. By M. VÈZES (*Compt. rend.*, **110**, 757—758).—When a concentrated solution of potassium platinonitrite is mixed with excess of hydrochloric acid and gently heated, nitrogen oxides are evolved and a yellow, crystalline powder separates, which is a mixture of potassium platinochloride and another salt of very similar appearance. The latter, however, crystallises in a different form, and the crystals act on polarised light; when heated alone, it evolves nitrogen oxides, and when heated in hydrogen, it yields an appreciable quantity of water and ammonium chloride. It is potassium nitrosoplatinochloride, K_2PtCl_5NO, and is analogous to the potassium nitrosorutheniochloride, K_2RuCl_5NO, described by Joly (Abstr., 1889, 352 and 678).

It is noteworthy that the percentage of potassium and platinum is practically the same in the platinochloride and the nitrosoplatinochloride. C. H. B.

Mineralogical Chemistry.

Mineral Synthesis. By E. WEINSCHENK (*Zeit. Kryst. Min.*, **17**, 486—504).—1. The author has prepared artificially a number of sulphides by the distillation of oxides with ammonium chloride and sulphur; a method first employed by Wöhler in 1836. The synthesis of a mineral, the author notes, can only be regarded as successful; not only when the chemical composition is copied, but also when the product has all the physical properties of the mineral. The sulphides prepared in sufficient quantity to enable the physical properties to be determined were iron pyrites, magnetite, cobalt sulphide, cupric sulphide, and galena. Nickel, manganese, and zinc gave unsatisfactory results, and silver sulphide could not be obtained in crystals by this method.

2. The minerals of the apatite group were prepared by the wet method. Apatite was obtained in well-developed crystals by heating a mixture of calcium chloride, ammonium phosphate, and excess of ammonium chloride in a closed glass tube at 150° to 180°. Other phosphates were obtained in a similar manner, as were also chlorarsenates and vanadates.

3. Oxides of metals that are more electropositive than copper were obtained in a crystallised condition by the action of metals on ammoniacal copper solutions. Magnetite, cuprite, and arnimite were obtained in this way. The last mineral was discovered by Weisbach (Abstr., 1888, 1259).

4. Sulphides were obtained by the decomposition of thiocyanates in acid solution. By the employment of ammonium thiocyanate, it is

possible to obtain an atmosphere of hydrogen sulphide at a high pressure. This method was employed for the preparation of a large number of sulphides and yielded a series of good results. The mixture in each case was heated at a temperature of 230° to 250° for four to six hours in a closed tube. In this way the author obtained galena from lead acetate, silver glance from silver acetate, covelline from copper sulphate, cinnabar from mercury chloride, orpiment from arsenious acid, troilite from iron ammonium sulphide, cuprous sulphide from cuprous chloride, mercurous sulphide from mercurous chloride, millerite from nickel sulphate solution, cobalt monosulphide from cobaltous chloride, and alabandine from manganese sulphate.

B. H. B.

Mercury Sulphates from a Furnace at Idria. By G. Seyfriedsberger (*Zeit. Kryst. Min.*, **17**, 433—444).—The mercury sulphates found in 1887 in pulling down a mercury furnace at Idria appear in two forms, a crust filled with geodes of small, pellucid crystals, and a white, crystalline, amorphous mass of globular structure. Both varieties are planted on yellow brick or mortar. The crystallised substance, which appears to be genetically the older of the two, gave on analysis 81·95 per cent. of Hg_2O and 16·72 per cent. of SO_3, and undoubtedly has the formula Hg_2SO_4. Its sp. gr. is 8·353. The crystalline substance on analysis yielded 27·02 per cent. of SO_3, and has consequently the formula $HgSO_4$. Its sp. gr. is 5·995. The crystallised sulphate is believed by the author to be trimetric, the observed forms being $\infty\bar{P}\infty$, $\infty\breve{P}\infty$, $0P$, ∞P, $\infty P\frac{2}{3}$, $\breve{P}\infty$, $\frac{1}{2}\bar{P}\infty$, $\bar{P}\infty$, $\frac{2}{3}\bar{P}\infty$, P.

B. H. B.

Supposed New Mineral from Montana. By R. Pearce (*Zeit. Kryst. Min.*, **17**, 402—403; from *Proc. Colorado Scient. Soc.*, **2**, 70).—A massive mineral found in the Gagnon mine, Butte, Montana, resembles bornite. Its hardness is 3·5 to 4, and its sp. gr. 4·95. Analysis gave the following results:—

S.	Cu.	Ag.	Zn.	Fe.	Insol.	Total.
20·51	41·10	24·66	9·80	2·09	1·02	99·18

The author is inclined to regard the mineral as a bornite in which copper is partly replaced by silver, and iron by zinc. B. H. B.

Artificial Silver-bismuth-glance. By R. Schneider (*J. pr. Chem.* [2], **41**, 414—424; compare this vol., p. 337).—When finely powdered bismuth sulphide is shaken with a feebly ammoniacal 1 per cent. solution of silver nitrate, practically no change occurs, a mere trace only of silver being thrown down as sulphide; but if the silver nitrate solution be neutral, the silver will be precipitated as sulphide and the bismuth converted into basic nitrate.

One gram of finely powdered potassium bismuth sulphide is put into a flask (60 c.c.) together with 25—30 c.c. of air-free water and a solution of 0·550 gram of silver nitrate to which ammonia has been added until the brown precipitate just redissolves; the flask is then filled up with air-free water and continually shaken. After 12—24

hours, the supernatant liquid is found to be free from silver; it is then decanted, and the residue shaken with air-free water for two days, then filtered, washed with water and absolute alcohol, pressed between filter-paper, and dried at 100°.

Thus prepared, silver-bismuth-glance has the composition Ag_2S,Bi_2S_3, and is a dark-grey powder; if crystals of bismuth sulphide are employed instead of powder in the above prescription, the resulting glance is crystalline and of the same form as the bismuth sulphide. It fuses without decomposition; the fused mass is light-grey and of metallic lustre; its fracture shows a homogeneous, leafy, crystalline structure; it is brittle, but not easily powdered. The powder is grey; its hardness is about 3·5; its sp. gr. at 15° is 6·96, that of the mineral being 6·92 (Rammelsberg). Cold nitric acid and hydrochloric acid do not attack it, but both acids decompose it when hot.

Artificial silver-bismuth-glance was also prepared by fusing silver sulphide and bismuth sulphide together in molecular proportion; the fused mass had all the above properties. A. G. B.

Sylvanite and Nagyágite from Nagyág. By W. HANKÓ (*Zeit. Kryst. Min.*, **17**, 514; from *Math. és term. tud. Értesitö*, **6**, 340—349). —Analyses of sylvanite (I) and nagyágite (II) from Nagyág gave the following results:—

	Au.	Ag.	Te.	Fe.	Cu.	Pb.	Sb.	S.	SiO_2.	Total.
I.	26·08	11·57	61·93	0·30	0·09	trace	—	—	0·32	100·34
II.	7·61	—	17·85	0·34	—	57·20	6·95	9·95	0·31	100·21

The sp. gr. of the sylvanite is 8·036, and that of the nagyágite 7·347. B. H. B.

Arsenical Pyrites from Wunsiedel. By K. OEBBEKE (*Zeit. Kryst. Min.*, **17**, 384—385).—In the marble quarry to the east of Wunsiedel, a fragment of a tin-white, hard, striated mineral has been found in a state of intimate association with the granular limestone. The mineral has a hardness of 6, and blowpipe tests indicated that it was arsenical pyrites. Analysis yielded—

As.	S.	Fe.	Total.	Sp. gr.
46·91	18·64	34·31	99·86	6·123

No notice has hitherto appeared of the occurrence of arsenical pyrites in the granular limestone of Wunsiedel. This mineral has, however, been found in the same rock at Auerbach. B. H. B.

Nickel Ore from Gosenbach. By HEUSLER (*Jahrb. f. Min.*, 1890, i, Ref. 206; from *Niederrhein. Ges. Bonn Sitzungsber.*, 1887, 67).—In the "Storch und Schöneberg" mine at Gosenbach, in the Siegen district, a nickel ore that occurs in small quantities gave on analysis the following results:—

Sb.	As.	Ni.	S.	Pb, Zn.
32·9	5·27	27·43	34·40	traces

The formula deduced from these results is $3NiS,(\frac{1}{5}As,\frac{4}{5}Sb)_2S_3$. Further investigation is necessary to determine whether the ore is a simple mineral.
B. H. B.

New Forms of Crystallised Silica. By MICHEL-LÉVY and MUNIER-CHALMAS (*Compt. rend.*, **110**, 649—652).—The authors describe the appearance and optical properties of certain forms of silica from the cretaceous rocks of the Paris basin. Two, to which they give the names *quartzine* and *lutecite*, are varieties respectively of chalcedony and quartz, from which they differ in the mode of development of the fibres and crystals, and in their optical properties.
C. H. B.

Pseudobrookite from Vesuvius. By J. A. KRENNER (*Jahrb. f. Min.*, 1890, i, Ref. 218—219; from *Földtani Közlöny*, **18**, 153—157).—On a piece of lava from the eruption of 1872, the author discovered small crystals of pseudobrookite, exhibiting the forms $\infty\bar{P}\infty$, $\infty\bar{P}2$, $\frac{1}{3}\bar{P}\infty$. The axial ratio is $a : b : c = 0·9683 : 1 : 1·0957$. The author notes the geometrical similarity with Guiscardi's guarinite, a mineral found in the sanidine bombs of Vesuvius. The analyses of the two minerals present no analogies, the formula of guarinite being CaO,SiO_2,TiO_2.
B. H. B.

Composition of Limestones from the "Montagnola Senese." By A. FUNARO (*Gazzetta*, **19**, 34—38).—A deep grey talcose argillaceous and calcareous schist of the triassic period, from Pietra Lata, near Ripostena, and an adjoining friable pulverulent rock, probably a product of the decomposition of the schist were first examined. They are both soluble with effervescence in dilute acids, leaving an abundant siliceous residue, and have the following compositiou :—

	$CaCO_3$.	$MgCO_3$.	Fe_2O_3.	P_2O_5.	Insoluble residue.
Schist	75·20	1·20	0·60	—	21·75
Do. decomposed	82·00	0·74	0·60	traces	15·00

The fact of the altered rock containing more lime and less silica than the original is an indication that the former contains detritus of neighbouring calcareous formations; this is confirmed by the presence of traces of phosphates in the decomposed rock.

Some limestones occurring near Montagnola, and a white earth lying between these rocks and the schists, gave the following results :—

Rock.	Locality.	$CaCO_3$.	$MgCO_3$.	SiO_2 and silicates.	Oxide of Fe.
1. Limestone	Fungaja ..	98·10	0·68	1·05	traces
2. ,,	,, ..	91·75	0·83	0·75	,,
3. ,,	S. Colomba	93·25	0·75	5·00	,,
4. White earth	Campo alla Pania ..	81·25	0·37	17·50	,,
5. White earth	Fungaja ..	38·80	0·57	56·25	1·00
6. ,,	Campo alla Pania ..	4·60	0·76	86·70	6·75
7. White earth	Campo alla Pania ..	0·50	0·57	95·20	0·75

(1) is a crystalline, (2) a friable, and (3) a spongy limestone; they are all adjacent rocks; the last two are probably derived from the decomposition of the first. (4) occurs between Campo alla Pania and Personata; it lies adjacent to the limestones, and is derived from their decomposition; it is a very fine, white earth, well adapted for the manufacture of porcelain, and has hitherto escaped notice. (6) and (7) are siliceous earths derived from the decomposition of the argillaceous schists.

A spongy, dolomitic limestone and a grey powder which occupied the interstices in the rock were next examined. The rock is grey, banded with white; when struck with the hammer, it emits a sulphureous and bituminous odour; the powder is ashy, non-adherent, and very finely grained. (1) is the solid rock from Val Maggiore, (2) is an altered rock from the same locality, (3) is a dolomitic powder from Cetunala, and (4) is the powder from the interstices of (2).

	$CaCO_3$.	$MgCO_3$.	Water.	Insoluble matter.
1	69·0	27·69	—	0·77
2	73·0	21·94	4·00	1·00
3	75·5	42·37	—	1·00
4	54·0	42·82	—	0·75

Analyses (3) and (4) exhibit the ordinary mode of decomposition of dolomitic rocks by loss of calcium carbonate; as this is, however, only the case at high temperatures (the reverse taking place at low temperatures), it would appear that the rock had been decomposed in deep strata, where the temperature is sufficiently elevated.

S. B. A. A.

Occurrence of Celestine and Barytes near Torda. By A. Koch (*Zeit. Kryst. Min.*, **17**, 510—511; from *Math. es term. tud. Értesitö*, **6**, 78—83).—Celestine and barytes occur in large quantities near Torda, in Torda-Aranyos Co., Hungary, in a bituminous limestone. The celestine is mined on an industrial scale. Three varieties occur with different specific gravities. The white, columnar variety has a sp. gr. of 3·89, whilst the bluish-white and the pellucid crystals have specific gravities of 3·93 and 3·94 respectively. The mineral is very pure, the mean of analyses of the different varieties giving the following results:—

SrO.	SO_3.	Total.
56·37	43·63	100·00

The barytes occurs in massive, white beds and veins, or in greyish-white, semi-transparent crystals. It is very pure, as is shown by the following analytical results:—

BaO.	SO_3.	Total.
65·47	34·40	99·87

B. H. B.

Mean Composition of the Celestine Bed of Koppánd. By E. Nyiredi (*Zeit. Kryst. Min.*, **17**, 515; from *Vegytani Lapok*, **6**, 56—58).—The author examined samples of about 9 lbs. in weight,

taken from different portions of the bed. The mean composition was found to be as follows:—

$SrSO_4$.	$CaSO_4$.	$CaCO_3$.	SiO_2.	Fe.	Total.
87·42	7·34	4·46	0·50	trace	99·72

B. H. B.

Crystallised Basic Copper Nitrate identical with Gerhardtite. By L. Bourgeois (*Compt. rend.*, **110**, 541—543).—If an aqueous solution of cupric nitrate and urea in equivalent proportions is heated in sealed tubes at 130°, it yields very thin, brilliant, pale, bluish-green leaflets of the basic nitrate, $Cu(NO_3)_2,3Cu(OH)_2$. It is insoluble in water, but easily soluble in dilute acids; sp. gr. 3·41. Its crystals are rectangular lamellæ derived from a rhombic prism of 94° 30′, and it is identical in composition and properties with the native basic cupric nitrate, *gerhardtite*, described by Brush and by Wells and Penfield.

Wells and Penfield, by heating copper nitrate solution with metallic copper at 150° in sealed tubes, obtained a basic nitrate of the same composition, but crystallising in forms derived from a monoclinic prism. The author was unable to obtain these crystals; under the conditions described, the product was identical with that obtained in presence of urea. The same product is formed when a solution of cupric nitrate is slowly concentrated. C. H. B.

Dahllite, a New Norwegian Mineral. By W. C. Brögger and H. Bäckström (*Zeit. Kryst. Min.*, **17**, 426; from *Öfv. vet. akad. förh.*, 1888, 493).—The new mineral was found at Ödegården, Bamle, Norway, as a fibrous crust on apatite. It is of a pale-yellow colour, but colourless in thin sections. Its sp. gr. is 3·053, and its hardness almost equal to that of apatite. Analysis yielded:—

CaO.	FeO.	Na_2O.	K_2O.	P_2O_5.	CO_2.	H_2O.	Total.
53·00	0·79	0·89	0·11	38·44	6·29	1·37	100·89

These results are in accord with the formula,

$$4(Ca,Fe,Na_2,K_2)_3P_2O_8,2CaCO_3 + H_2O.$$

The microscopic examination indicated that the mineral was quite unaltered, and homogeneous. This new mineral, the only combination of a phosphate and a carbonate yet known, has been named dahllite, in honour of the well known mineralogists Tellef and Johann Dahll. B. H. B.

Vivianite from the Szentes Artesian Well. By K. v. Muraközy (*Zeit. Kryst. Min.*, **17**, 521; from *Földtani Közlöny*, **18**, 465—466).—The mineral, which was obtained from the artesian well of the town of Szentes, Csongrád Co., Hungary, at a depth of 160 metres, was found in the form of grains in the clay. On analysis it gave the following results:—

FeO.	Fe_2O_3.	P_2O_5.	H_2O.	SiO_2.	Total.
40·00	0·83	26·86	24·37	7·94	100·00

B. H. B.

Delvauxite and Diadochite from Vysočany, Bohemia. By F. KOVÁŘ* (*Listy Chem.*, 14, 1—6, 36—42).—The author has analysed six samples of delvauxite from diluvial clays, and confirms the formula $2(Fe_2P_2O_8),Ca_3P_2O_8,4Fe_2(OH)_6 + 9H_2O$. Diadochite from the same locality was found to correspond with the formula $3Fe_2P_2O_8,2Fe_2(SO_4)_3,Fe_2(OH)_6 + 36H_2O$. Plattner finds the same formula with $45H_2O$, Cèsar $33H_2O$. Diadochite has evidently been formed from delvauxite, and often an intimate mixture of both kinds of minerals is found. B. B.

Crystals of Sarkinite. By G. FLINK and A. HAMBERG (*Zeit. Kryst. Min.*, 17, 431—432; from *Geol. fören. förh.*, 10, 380).—In the Harstig mine, at Pajsberg, in Sweden, the authors found a crystallised mineral, which on analysis presented great similarity to two minerals already known, sarkinite and polyarsenite. Indeed, it is probable that these three minerals are identical, as their hardness, colour, lustre, and composition are the same. Igelström's name of polyarsenite has the priority, but it is unsuitable in that the mineral is an arsenate and not an arsenite. The author's therefore prefer Sjögren's name of sarkinite. The analytical results were as follows:—

MnO.	CaO.	MgO.	H_2O.	As_2O_5.	P_2O_5.	Total.
51·92	1·22	0·38	3·48	41·50	trace	98·42

Formula, $(MnO)_4As_2O_5 + H_2O$. The mineral crystallises in the monosymmetrical system, the axial ratio being $a : b : c = 2·0013 : 1 : 1·5880$; $\beta = 62° 14'$. The forms observed were $\infty P\infty$, $0P$, ∞P, $2P\infty$, P. The colour is pink, the hardness 4 to 5, and the sp. gr. 4·22. B. H. B.

Serpentine from Finland. By Miss M. TCHAJTCHINSKY (*Zeit. Kryst. Min.*, 17, 526; from the *Proc. Soc. Naturalists, St. Petersburg*, 19, 3).—A series of light (I to III) and dark (IV to VI) varieties of serpentine from Hopunwara, near Pitkäranta, in Finland, were analysed with the following results:—

	I.	II.	III.	IV.	V.	VI.
SiO_2....	38·07	39·66	39·12	41·02	35·90	39·51
Al_2O_3...	3·33	1·71	1·26	1·11	1·69	0·41
FeO....	3·26	2·70	2 01	1·81	1·32	1·28
Fe_2O_3...	0·61	0·57	0·55	0·32	0·72	0·41
CaO....	1·20	1·46	2·63	1·05	6·09	2·79
MgO...	38·77	40·86	39·48	41·69	38·16	41·46
H_2O....	13·83	13·51	14·36	13·17	12·11	10·76
CO_2....	—	—	—	0·66	4·49	4·03
Total...	99·07	100·47	99·41	100·83	100·48	100·63
Sp. gr...	2·56	2·56	2·55	2·52	2·56	2·57

B. H. B.

* Read Kovaarsh.

Serpentine from Montville, New Jersey. By G. P. MERRIL (*Zeit. Kryst. Min.*, **17**, 418—419; from *Proc. U.S. Nat. Museum*, 1888, 105—111).—The author has investigated the origin of the well-known Montville serpentine. It occurs in association with crystalline dolomite. The centre of the masses usually consists of a white or grey mineral, often erroneously believed to be dolomite, which, as a matter of fact, consists of diopside, as is shown by the following analyses:—

	SiO_2.	MgO.	CaO.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	H_2O.	Total.
I.	51·45	18·43	24·02	2·94	1·06	0·96	trace	1·08	99·94
II.	40·23	39·46	—	2·18	4·02	trace	—	14·24	100·13
III.	54·21	19·82	24·71	0·59	0·20	0·27	—	0·14	99·94
IV.	42·38	42·14	—	0·07	0·97	0·17	—	14·12	99·85

I, Grey pyroxene; II, green serpentine, the product of its decomposition; III, white pyroxene; and IV, yellow serpentine, the product of its decomposition.

The serpentine contains a fairly high proportion of water. The lime set free by the alteration of the diopside is recrystallised as granular calcite of a bluish tint or in fibres. Free silica was not observed, and it may therefore be concluded that sufficient magnesia was present to combine with the excess, and to form serpentine. The author is of opinion that further investigations of small distinct masses of serpentine, enclosed in calcareous or slaty rocks, will indicate a similar mode of origin. B. H. B.

Nephrite and Jadeite. By F. W. CLARKE and G. P. MERRIL (*Zeit. Kryst Min.*, **17**, 413; from *Proc. U.S. Nat. Museum*, 1888, 115—130). The authors have submitted the ethnological specimens of jade, nephrite, &c., in the U.S. National Museum, to careful examination. The following are selected from the numerous analyses given:—

	1.	2.	3.	4.	5.
SiO_2	56·01	58·11	58·18	59·18	58·33
Al_2O_3	1·98	0·24	23·53	22·96	21·63
Fe_2O_3	—	5·44	—	} 1·87	{ 1·71
FeO	6·34	0·38	1·67		{ 0·73
MnO	—	trace	—	—	—
CaO	12·54	12·01	2·35	1·52	4·92
MgO	21·54	21·97	1·72	0·67	3·09
Na_2O	—	—	11·81	12·71	8·13
K_2O	—	—	0·77	trace	0·22
Ignition	1·91	1·78	0·53	0·90	0·93
Total	100·32	99·93	100·56	99·81	99·69
Sp. gr.	2·989	—	3·190	3·32	3·27

Nos. 1 and 2 are analyses of jade from Alaska, found *in situ* in the Jade Mountains, about 150 miles from the Kowak river. Numerous varieties are found at this locality, but microscopic examination proves that they are all nephrites. The authors therefore conclude

that the jade tools found in Alaska have not been derived from Siberia, as has hitherto been supposed. Jade tools from the State of Oaxaca, in Mexico (Analysis 3), are similar in composition to Damour's jadeite. The series of jade tools from Central America are shown to belong to three groups. The first is jadeite, more or less impure; the second has the sp. gr. of quartz, and also belongs partly to this species; whilst the third includes those of low specific gravity, and is characterised by softness. Jadeite from Sardinal (Analysis 4) was found under the microscope to be a finely granular aggregate of colourless crystals of pyroxene, and a specimen of this mineral from Culebra (Analysis 5) consisted of a fibrous aggregate of colourless elongated fibres and scales. Nephrite and jadeite may be distinguished by the fact that the former is fibrous and massive, whilst the latter is distinctly granular. The authors deny that nephrites from different localities may be distinguished under the microscope.

B. H. B.

Constitution of certain Zeolites. By C. Doelter (*Jahrb. f. Min.*, 1890, i, Mem. 118—139).—The author has prepared artificially a number of zeolites, with a view to obtain information as to their constitution and mode of formation. The zeolites he has prepared synthetically are apophyllite, okenite, chabasite, heulandite, desmine, laumontite, thomsonite, analcime, natrolite, scolezite, and prehnite. All these zeolites are soluble in water, especially when containing carbonic acid, at an elevated pressure, and can thus be recrystallised. The temperatures employed amounted to 120° to 160°. Several of the zeolites are soluble in liquid carbonic anhydride at a much lower temperature (25°). Analcime, heulandite, and more rarely chabasite, may be obtained from solutions of salts containing silica, alumina, calcium carbonate, or sodium carbonate, in closed tubes at a temperature of 130° to 190°. All zeolites consist of a silicate resembling nepheline, pyroxene, or felspar, to which meta- or orthosilicic acid is added. In most cases, the zeolites also contain varying quantities of water of crystallisation, the number of molecules of water being dependent on the temperature. The water of crystallisation may be driven off by increasing the temperature, but in most cases it may be taken up again. The hydrates varying with the temperature may possess different crystalline forms. A given number of molecules of water cannot be driven off without effecting the decomposition of the compound. This water is present as silicic acid. By melting and recrystallising, the silicate that forms the basis of the zeolites may in several cases be obtained. This silicate is an ortho- or metasilicate. The formulæ of the zeolites may be tabulated thus—

Apophyllite ..	$Ca(K_2)SiO_3 + H_2SiO_3 + H_2O$.
Okenite......	$CaSiO_3 + H_2SiO_3 + H_2O$.
Pectolite	$CaNa_2Si_2O_6 + H_2SiO_3$.
Chabasite....	$CaAl_2Si_2O_8 + 2SiO(OH)_2 + 6H_2O$.
Heulandite...	$CaAl_2Si_4O_{12} + 2SiO(OH)_2 + 3H_2O$.
Desmine.....	$CaAl_2Si_4O_{12} + 2SiO(OH)_2 + 4H_2O$.
Laumontite ..	$CaAl_2Si_2O_8 + 2SiO(OH)_2 + 2H_2O$.
Thomsonite ..	$2\{(CaAl_2Si_2O_8)(Na_2Al_2Si_2O_8)\} + 5H_2O$.

Analcime	$Na_2Al_2Si_2O_8 + 2SiO(OH)_2$.
Natrolite	$Na_2Al_2Si_2O_8 + Si(OH)_4$.
Scolezite	$CaAl_2Si_2O_8 + Si(OH)_4 + 2H_2O$.

B. H. B.

Analyses of Idocrase. By G. LINDSTRÖM (*Zeit. Kryst. Min.*, **17**, 430—431; from *Geol. fören. forh.*, **10**, 287).—The varieties of idocrase analysed by the author were (1) jewreinowite, from Frugard, and (2) cyprine, from Telemarken.

The results were as follow:—

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CuO.	CaO.	MgO.
I.	39·15	0·19	18·27	1·14	1·57	0·10	0·18	34·98	2·39
II.	37·90	0·26	19·47	0·40	0·21	0·91	0·73	36·06	2·17

	K_2O.	Na_2O.	F.	H_2O.	Total.
I.	0·07	0·06	1·73	0·55	100·38
II.	0·11	0·14	1·72	0·67	100·75

The idocrase from Ala contains no fluorine, whilst that from Monzoni contains 0·31 per cent., as well as traces of boric acid.

B. H. B.

Anorthite from Miyakejima, Japan. By Y. KIKUCHI (*Zeit. Kryst. Min.*, **17**, 421; from *J. Imp. Coll. of Sci., Tokyo*, **2**, 31).—The volcano of the island of Miyake consists of anorthite-basalt, rendered porphyritic by crystals of anorthite, which also occur in considerable quantities loose. The angles made by the direction of extinction with the edge formed by the faces 0P and $\infty\breve{P}\infty$ is $-38°$ to $-40°$ on cleavage plates taken parallel to 0P, and $-40°$ to $-41°$ on plates parallel to $\infty\breve{P}\infty$. The mineral has a sp. gr. of 2·761, and yielded on analysis the following results:—

SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.	H_2O.	Total.
44·03	36·80	19·29	0·20	0·23	0·12	100·67

B. H. B.

Phillipsite from Somoskö. By A. KALECSINSZKY (*Zeit. Kryst. Min.*, **17**, 521—522; from *Jahrb. köngl. ung. geol. Anstalt*, 1888, 123—131).—Well-developed, white crystals of phillipsite from cavities in the basalt of Somoskö, Nógrád Co., Hungary, gave on analysis the following results:—

SiO_2.	Al_2O_3.	CaO.	K_2O.	H_2O.	Total.	Sp. gr.
49·65	21·88	6·99	5·28	16·16	99·96	2·201

B. H. B.

Artificial Production of Rock-forming Minerals. By K. KOZIOROFFSKI (*Zeit. Kryst. Min.*, **17**, 527—528; from *Com. Univ. Warsaw*, 1, 1—9).—The author has melted together SiO_2, Al_2O_3, $CaCO_3$, $MgCO_3$, Na_2CO_3, $FeCO_3$, Fe_2O_3, and Fe_3O_4 in various proportions at a white heat in a Siemens crucible furnace for 30 to 48 hours. A mixture, having the composition of a basalt (3 olivine, 1 augite, 3 labradorite, 0·5 Fe_9O_4), was only partially melted. The melted portion was crystalline, and consisted chiefly of polysynthetic

twin-crystals of a plagioclase, probably oligoclase. Another mixture having the composition of ophite (1 anorthite and 2 augite) yielded crystals of plagioclase, spinel, and magnetite, in an amorphous glass. A mixture having the composition of a trachyte (1 andesine, 10 orthoclase, and 2 augite) yielded an amorphous-green glass. On heating this glass for 10 days, sphærolites were formed. These consisted partly of long, radiating needles of an acid felspar, and partly of minute crystals of augite. Leucite was also formed.

Fayalite crystals from a mill-cinder from an ironworks near Moscow were found to have the following composition:—

SiO_2.	FeO.	Total.
31·69	67·78	99·47

Under the microscope a number of magnetite inclusions were observed. B. H. B.

Solubility of some Substances in Sea-water. By J. THOULET (*Compt. rend.*, **110**, 652—654).—Pumice, shells, coral, and globigerinæ, in somewhat small grains, were left in contact with sea-water and distilled water for several months, the water being renewed every week. The solids were then washed with equal volumes of distilled water, dried, and weighed. The loss of weight gave the quantity which had been dissolved. The experiments were made in the dark in order to avoid the development of algæ. The solubility of the four substances in distilled water is very small, but is considerably greater than their solubility in sea-water. This difference is probably due in part to the fact that distilled water always contains carbonic acid, whereas sea-water is alkaline. C. H. B.

Organic Chemistry.

Results and Aims of Stereochemical Research. By V. MEYER (*Ber.*, 23. 567—619).—The author first gives an historical review of the development of stereochemical or space formulæ. Although it was long tacitly understood that the four hydrogen-atoms in methane must be arranged symmetrically in space around the carbon-atom, Van't Hoff and Le Bel were the first to point out the important advantages that are derived by the adoption of the tetrahedral symbol for the carbon-atom to which the above view naturally leads. By this method they were able to explain the isomerism of a number of compounds, such as the lactic acids, the formulæ of which contain asymmetrical carbon-atoms, and therefore in space are capable of two enantiomorphic methods of representation. Geometrical isomerism is then possible amongst substances containing an asymmetrical carbon-atom, and it was likewise shown that such geometrical isomerides frequently show optical activity. A distinct connection was traced

between the presence of an asymmetrical carbon-atom and the optical activity of the substance in which it occurs; so that we are now able to say that, although a substance containing an asymmetrical carbon-atom may not be optically active, the reverse is never true; and if a substance has optical properties, it will be certain to contain an asymmetrical carbon-atom. Not only so, but in the case of a number of substances containing asymmetrical carbon-atoms, and yet optically inactive, the inactivity has proved to be only apparent and due to the fact that in each case the substance in question was really a mixture of two isomerides of equal but opposite rotatory power; for instance, the propylene glycols investigated by Le Bel, mandelic acid by Lewkowitsch, and Ladenburg's inactive conine. Some facts, however, as for instance the occurrence of the two inactive hydrobenzoïns, still remain to be explained.

An explanation of the occurrence and stability of ring compounds has also been made possible by the adoption of the tetrahedral carbon-atom. As Baeyer has pointed out, the angles of a regular pentagon are very nearly equal to those which the lines representing the directions of the valencies in the tetrahedral carbon-atom make with one another; hence by joining the valencies of five such carbon-atoms, one with another, a closed ring would practically be obtained. It will be seen that the carbon-atoms in this case are assumed to lie in a plane. That in benzene (the most stable and readily formed of the ring compounds) six and not five carbon-atoms are present, is explained by the author as due to the fact that only a very slight tension would be necessary in the introduction of this additional carbon-atom, whereas the stability of the compound would be enormously increased by the symmetry thus given to the molecule. In support of this, it is pointed out that it is impossible to arrange the valencies symmetrically in a ring of only five carbon-atoms. Baeyer's assumption that in the case of the formation of double and treble linking the valencies are subject to tension, and the compounds formed in consequence unstable, is one with which the author does not agree. He points to the formation of acetylene directly from carbon and hydrogen at white heat. The instability of such compounds as the polyacetylenecarboxylic acids and diacetylene is not surprising when one remembers the remarkable constitution of these substances, and may not be due to the treble linking which they contain. It may rather be caused by a tendency for the atoms to rearrange themselves into more stable configurations, just as the unstable silver oxalate passes on explosion into silver and carbonic anhydride.

Passing on to the work of Wislicenus, the author points to the development of the view that carbon-atoms, united by a single bond, are free to rotate, and, therefore, only take up the most stable position; whereas in the case of a double bond this rotation is prevented, and the atoms compelled, in some cases, to take up positions of unstable equilibrium. On the assumption that the specific affinities of the groups united with the carbon-atoms determine the stability or instability of alternative arrangements in the latter case, the actual positions in space occupied by the above groups with relation to one another may, in some cases, be predicted. The well-known instance

of fumaric and maleïc acids is here alluded to. The conversion of maleïc into fumaric acid by the action of hydrobromic acid cannot, however, be explained on Wislicenus' assumption of the intermediate formation of a monobromosuccinic acid, because, as Anschütz has shown, such an acid would be a very stable compound, and would not undergo change into fumaric acid under the conditions of the above transformation. The formula given by Anschütz (Abstr., 1887, 916) for maleïc acid is, however, untenable, as it would lead to the assumption of the existence of two isomeric succinic acids, for which there is no experimental evidence, and, as far as the structure of the fumaric and maleïc acids is concerned, the views of Wislicenus must be considered correct.

Grave objections have, however, been raised to the view that carbon-atoms united by a single affinity are free to rotate, and will, therefore, only take up the most favourable position, by the work of the author and Auwers on the benzildioximes (Abstr., 1888, 597; 1889, 403, 713). Only one such compound should be known, since a benzildioxime contains no asymmetrical carbon-atom, and the carbon-atoms are only united by a single bond, and therefore should be free to rotate and to take up the one most favourable position. In spite of these facts, three isomeric benzildioximes have up to the present been discovered, and the existence of these isomerides can only be explained by assuming that in this case free rotation of the carbon-atoms about the bond of union does not take place, and that in consequence three different stable arrangements are possible corresponding with the three isomerides. The discovery of the isobenzaldoxime by Beckmann, containing the group —NH·O—, at first appeared to open out the possibility of this group being also present in the benzildioximes, and the isomerism being therefore due to differences in structure; but this has since been disproved by Auwers and Dittrich (Abstr., 1889, 1192). There is now no doubt as to the structural identity of the benzildioximes, whatever be the explanation of their isomerism.

Goldschmidt (this vol., p. 253) considers Beckmann's benzaldoximes as identical in structure, since both combine with phenylcarbimide to form isomeric additive products. There is, however, no *a priori* reason why a substance containing the group —NH·O— should not combine with phenylcarbimide as readily as one containing the NOH-group, and therefore the above cannot be held to prove anything. The author has further evidence that Beckmann's isobenzaldoxime contains the imido-group, since the methyl salt of this compound, on treatment with hydrochloric acid, yields β-methylhydroxylamine NHMe·OH, melting at 85—90°, whereas the α-benzaldoxime yields α-methylhydroxylamine NH_2·NMe, melting at 148°.

Hantzsch and Werner (this vol., p. 348) have put forward an explanation of the occurrence of isomeric benzil mono- and dioximes which is based on the assumption that the nitrogen-atom may be represented as a tetrahedron, and that when a nitrogen-atom is united by two of its valencies to a carbon- or second nitrogen-atom, we may have cases of isomerism similar to that of fumaric and maleïc acids. The isomerism of the benzaldoximes is explained in accordance with

this view, but, as above shown, the structure of these two compounds is in all probability not identical, and therefore the explanation and support it offers to the hypothesis fall to the ground. Again, all unsymmetrical oximes of the formula OH—N:CXY should exist in two isomeric forms; but this is altogether contradicted by experience. Auwers has undertaken a special investigation of the oxime OH·N:CPh·C_6H_4Me, but without being able to detect signs of the formation of an isomeride. Whilst the oximes of benzil occur in isomeric forms, those of phenanthraquinone exhibit no isomerism, according to the author's view limited rotation being possible in the first case but not in the second, as will be seen by a comparison of the two formulæ $\begin{array}{c}\text{Ph·C:O}\\ | \\ \text{Ph·C:O}\end{array}$ and $\begin{array}{c}C_6H_4\text{·C:O}\\ | \quad\quad | \\ C_6H_4\text{·C:O}\end{array}$. According to the views of Hantzsch and Werner, however, a corresponding number of isomerides should be obtained from each, which is not the case. Hantzsch and Werner also offer no explanation of the non-occurrence of isomerism in the dioxime derived from diacetyl, which has been explained by the author as due to the fact that whereas the C_6H_5- and NOH-group are in an equal degree negative in character, this is not the case with Me and NOH.

If the tetrahedral representation were tenable for the nitrogen-atom, we should have to assume that substituted ammonias can exist in the isomeric forms $N\begin{array}{l}\diagup H\\ -a\\ \diagdown b\end{array}$ and $N\begin{array}{l}\diagup H\\ -b\\ \diagdown a\end{array}$, but this is not so. We must therefore assume that in ammonia the hydrogen-atoms are placed symmetrically with regard to the nitrogen-atom, and this can only find expression in a plane formula. In ring compounds, such as pyridine, the valencies probably no longer lie in a plane, since they replace those of a carbon-atom; but of this little can as yet be ascertained.

In conclusion, the author touches on one or two questions connected with the possible space representation of the oxygen- and sulphur-atoms, and he urges the necessity of the employment of space formulæ and of no longer regarding the atoms as mere points without shape or dimensions. H. C.

Chemical Constitution of Carbon Compounds and the sign and variations of their Rotatory Power. By P. A. GUYE (*Compt. rend.*, **110**, 714—716).—Admitting that the valencies of carbon are directed towards the solid angles of a regular tetrahedron, and calling the six planes of symmetry which characterise the compound CR_4 the *planes of carbon symmetry*, it is evident that so long as the carbon remains symmetrical the centre of gravity of the molecule will be found in one, at least, of these planes. On the other hand, if the carbon becomes asymmetrical, the centre of gravity will be outside these planes. In the first case, the *product of asymmetry*, that is, the product of the distances of the centre of gravity of the molecule from each of the planes of symmetry, will be zero; in the second case, it will have a definite value. If the signs + and − are given to these distances, measured from one side or the other of each plane of

symmetry, the *product of asymmetry* will be positive or negative, according to circumstances.

It follows that whenever the displacement of one radicle by another leaves the centre of gravity on the same side of the planes of symmetry, the rotatory power of the compound will retain the same sign; if, as a result of substitution, the centre of gravity is removed further away from the planes of symmetry, the rotatory power will be increased; if it is brought nearer to the planes, the rotatory power will be reduced; if, as a result of substitution, the centre of gravity is displaced from one side of one of the planes of symmetry to the other side, the sign of the optical rotation will be changed.

These deductions are experimentally verified in the case of amyl alcohol and amyl chloride, bromide, iodide, cyanide, and acetate; mono-, di-, and tri-amylamines and their hydrochlorides; asparagin and aspartic acid and their salts and compounds with acids; dextrotartaric acid and its derivatives, malic acid and its derivatives, and many other compounds.

The increase in rotatory power consequent on a removal of the centre of gravity further away from the planes of symmetry is well shown in the case of the ethereal salts of tartaric acid.

	Methyl.	Ethyl.	Propyl.	Isobutyl.
$[\alpha]_D =$	$+2 \cdot 14°$	$+7 \cdot 66°$	$+12 \cdot 44°$	$+19 \cdot 87°$

In dibenzoyltartaric acid the centre of gravity passes to the opposite side of the plane, cutting the edge COOH—OBz, and consequently dibenzoyltartaric acid is lævogyrate, $[\alpha] = -117 \cdot 68°$.

The substitution of alkyl radicles for the basic hydrogen leaves the centre of gravity on the same side of that particular plane, but reduces its distance, and consequently the rotatory power of the ethereal salts diminishes as the molecular weight of the alkyl radicle increases.

	Methyl.	Ethyl.	Isobutyl.
$[\alpha]_D =$	$-88 \cdot 78°$	$-60 \cdot 02°$	$-41 \cdot 92°$

Diacetyltartaric acid is lævogyrate ($[\alpha]_D = -23 \cdot 14°$) for a similar reason, but in this case the introduction of a sufficiently heavy alkyl radicle carries the centre of gravity to its original side of the plane of symmetry, and the sign of rotation changes.

	Methyl.	Ethyl.	Propyl.	Isobutyl.
$[\alpha]_D =$	$-14 \cdot 29°$	$+1 \cdot 02°$	$+6 \cdot 52°$	$+10 \cdot 29°$

C. H. B.

Limitation of the free Rotation of singly bound Carbon-atoms. By C. A. Bischoff (*Ber.*, **23**, 623—630).—Assuming that by the accumulation of alkyl groups in a molecule, such as that of succinic acid, the carbon-atoms are caused to approach one another (compare this vol., p. 741), it is possible that the vibrations of some of the atomic complexes of which the molecule is composed may become limited, owing to interference with one another, and two systems which have hitherto been regarded as capable of free rotation

round a common axis might, under certain conditions, have their power of rotation limited; in other words, configurations which are at present looked on as identical, because the one can be converted into the other by simple rotation, would become dissimilar, and compounds possessing these two configurations would differ from one another in properties in a manner somewhat analogous to, but probably to a smaller extent than that in which geometrically isomeric substances differ from one another.

This hypothesis is similar to that put forth by Riecke and V. Meyer, but it differs from the latter in assuming that the limitation of free rotation is brought about in the manner described above, and not by the purely chemical nature of the substituting radicles.

If energy is supplied to a system the rotation of which is supposed to be limited in this way, it may be conceived that the impact of any two groups which interfere with one another may become powerful enough to force asunder again those carbon-atoms, the mutual approach of which has led to interference; in this way the one configuration would be converted into the other.

The author names isomerism of this nature "dynamical isomerism," and explains his hypothesis with the aid of diagrams. The fact which led to the origination of this hypothesis is the formation of two ethyldimethylsuccinic acids by the hydrolysis of ethyl ethylisobutenyltricarboxylate (this vol., p. 743).

In accordance with the above theory, propyldimethyl-, isopropyldimethyl-, and benzyldimethylsuccinic acid can also exist in two dynamically isomeric forms; the results of experiments on benzyldimethylsuccinic acid are described in another paper (this vol., p. 774).

F. S. K.

Fluoroform. By MESLANS (*Compt. rend.*, **110**, 717—719).—Two parts of iodoform, two parts of silver fluoride, and one part of chloroform are mixed in a flask, which is cooled to 0° and is connected with a lead worm, kept at −23°, followed by a U-tube containing silver fluoride heated at 100°. The temperature of the flask is allowed to rise gradually, and the gas which is evolved is collected over mercury. It is purified from chloroform vapour by prolonged contact with fragments of dry caoutchouc, and from carbonic oxide by means of a solution of cuprous chloride in hydrochloric acid. The product is a colourless gas, with a pleasant odour resembling that of chloroform; it burns with difficulty with a blue flame and abundant evolution of hydrogen fluoride; it is only slightly soluble in water, chloroform, or benzene, but alcohol dissolves about five times its own volume. Its sp. gr. is 2·445, and it liquefies under a pressure of 40 atmos. at 20°; if the pressure is suddenly released, it solidifies.

This gas is *fluoroform*, CHF_3; when heated with alcoholic potash at 160°, it yields potassium formate and fluoride. Sodium heated in the gas burns brilliantly, with deposition of carbon and sodium fluoride and formation of methane.

When silver fluoride and iodoform react in absence of chloroform, much heat is developed, iodine is liberated, and a fluoriodoform is produced.

C. H. B.

Determinations of Molecular Weights of Organic Compounds by Raoult's Method. By E. PATERNO and R. NASINI (*Gazzetta*, **19**, 195—209).—*Polymeric Compounds.*—Ethyl cyanate and cyanurate in a benzene solution gave results agreeing with the molecular formulæ EtCNO and $Et_3(CNO)_3$. Metacinnamene, obtained by the spontaneous polymerisation of pure cinnamene, gave in a benzene solution a result corresponding with $(C_8H_8)_3$; more concentrated solutions (3—9 per cent.) gave a value intermediate between $(C_8H_8)_4$ and $(C_8H_8)_5$.

Isomerides, &c.—Apiole and isoapiole in benzene solution both gave results agreeing with the formula $C_{12}H_{14}O_4$. Ciamician and Silber's view that these compounds are not polymerides is thus confirmed.

Urimidosuccinic Acids.—Both the lævogyrate and the inactive varieties gave in dilute aqueous solution a result corresponding with the molecular formula $C_5H_6N_2O_4$.

Benzene Hexachlorides.—The α-compound gave a normal result in acetic acid and concentrated benzene solutions; the β-compound is isomeric with it.

Diphenic Anhydride.—The numbers obtained from the acetic solution point to the formula $(C_6H_4{\cdot}CO)_2O$ as molecular, but it would appear that the anhydride is dissociated by solution in acetic acid.

Naphthalene Picrate.—Concentrated acetic solutions give approximately normal figures; dilute solutions indicate that complete dissociation into naphthalene and picric acid has taken place. Normal results were obtained from benzile, carvacrol, carvacrol hydrosulphide, and from amarine in benzene solutions, and from dimethylquinol, benzoïn, dehydracetic acid and amide, and benzimidobenzoate in acetic acid solutions. Thymoquinone and camphoric chloride gave normal results, but in the case of camphoric chloride it was apparent that some dissociation had taken place. Usnic acid, both in acid and in benzene, and anilide in a dilute benzene solution gave abnormal results, probably due to some decomposition.

Colloïdal Substances.—2 per cent. solutions of albumin and gelatin barely reduced the freezing point by 0·01°; it would therefore appear that these colloïds have an extremely complicated molecular structure. The calculations from the observed data were all made by Raoult's method.

The behaviour of paraldehyde, anethoïl, phenol, and bromoform as solvents was examined; the results obtained with paraldehyde were irregular on account of the readiness with which it undergoes partial dissociation into aldehyde; anethoïl gave more uniform results, but the experiments were discontinued on account of its peculiar behaviour; the addition of a crystal to the mass when cooled a few tenths of a degree below the freezing point induces congelation, as with other solvents, but instead of the temperature rising at once to the freezing point, it continues to descend with extreme slowness, and then returns. Bromoform could not be obtained sufficiently pure; experiments with phenol-derivatives are still in progress. The author concludes that paraldehyde and, to a lesser extent, anethoïl may be useful in special circumstances. S. B. A. A.

Products of the action of Propionitrile on Chlorides of the Fatty Acids in presence of Aluminium Chloride.—Triethyl Tricyanide. By R. OTTO and J. TRÖGER (*Ber.*, **23**, 759—768).—In a preliminary notice (Abstr., 1889, 957) the authors stated that by the action of aluminium chloride on a mixture of propionitrile and propionic chloride, propionylpropionitrile appeared to be formed, which at once took up the elements of water, forming propionylpropionamide. In the further course of the investigations, acetic chloride was substituted for propionic chloride, and the same compound obtained as before. This formation shows that the constitution previously assigned to the substance is incorrect and further investigation has shown that it is *dipropionamide*, $NH(CO{\cdot}CH_2{\cdot}CH_3)_2$. This has been confirmed by a direct comparison of the compound in question with the dipropionamide obtained by the usual reactions.

Dipropionamide crystallises in rectangular tablets or long needles which melt at 153—154°, sublime readily, and distil without decomposition at 210—220°. It is sparingly soluble in cold, readily in hot, water, and still more readily in alcohol. It is quickly converted into propionic acid and ammonia by both potassium hydroxide and dilute sulphuric acid. Its formation in the above reaction is probably due to the fact that a portion of the propionitrile is reduced to propionamide, which, by the action of the hydrochloric acid formed from the aluminium chloride, passes into dipropionamide.

Triethyl tricyanide, like the tricyanides obtained by Krafft and Hansen (Abstr., 1889, 696), has basic properties, and may be converted into a hydrochloride by passing hydrogen chloride over the fused compound. By the action of water this readily passes into ammonium chloride and propionic acid, on which account no platinochloride could be prepared. According to T. Weyl, triethyl tricyanide has a poisonous action on dogs and guinea-pigs, resembling that of certain ptomaïnes. H. G. C.

Molecular Weight of the solid α-Dichloropropionitrile. By R. OTTO (*Ber.*, **23**, 836—837).—The solid compound (m. p. 73—74°) obtained by the action of dry chlorine on propionitrile (*Annalen*, **116**, 195; **132**, 181) has the molecular formula $(C_3H_3Cl_2N)_3$, as is proved by molecular weight determinations by Raoult's method in glacial acetic acid solution. F. S. K.

Coloration of Organic Substances by Thiocyanic Acid. By C. PARENTI (*Gazzetta*, **19**, 175—179).—The reddish coloration which thiocyanic acid imparts to animal and vegetable tissues is generally held to be due to the presence of minute traces of iron; this is denied by Miguel (Abstr., 1877, 457), who found that paper presumably free from iron acquired a red coloration on exposure to the vapour of thiocyanic acid, although it was not coloured by the aqueous acid. The author has repeated this experiment, and finds that paper in which no iron can be detected by analysis exhibits the phenomena described by Miguel, but if it is previously digested for several days in pure dilute hydrochloric acid, then thoroughly washed and dried, it is no longer affected by the acid. On the other hand, if the purified paper

or cotton cloth is wetted with water to which one drop of an extremely dilute solution of ferric chloride has been added, and dried, it regains its original character. It follows that the coloration is due to the presence of traces of iron, which are so small that they are only detected by the extremely delicate action of the fumes of thiocyanic acid. The coloration is not affected by anhydrous ether, absolute alcohol, benzene, carbon bisulphide, or chloroform, but it is destroyed by excess of water; a drop of a mixture of ether or alcohol and water leaves a stain, which, on drying, becomes first green and then white. This reaction is so delicate that it may be used as a test for the presence of water in ether or absolute alcohol; in the last case the test must be made in a closed vessel, as absolute alcohol abstracts sufficient moisture from the air to give the green stain.

Miguel's distinction between the red coloration given to paper imbued with ferric chloride by fumes of thiocyanic acid and the yellowish-red coloration given by the aqueous acid is due to the action of the liberated hydrochloric acid, which, in presence of water, facilitates the decomposition of thiocyanic acid into perthiodicyanic acid.

S. B. A. A.

Purification of Alcohol. By E. WALLER (*Chem. News*, **61**, 53—54).—The alcohol is agitated with powdered potassium permanganate until distinctly coloured, and after some hours treated with a pinch of pulverised calcium carbonate. It is then carefully distilled, but not to dryness, and is collected for use when the distillate ceases to give a yellow coloration with strong potash or soda within 20 or 30 minutes.

D. A. L.

Etherification by Uranium Salts. By O. POHL (*Listy Chem.*, **14**, 104—105).—On pouring amyl alcohol over uranium nitrate, the latter is decomposed by the action of light, and, at the ordinary temperature, valeraldehyde, free valeric acid, amyl valerate, and amyl nitrate, together with some reduction products containing oxides of uranium, are formed. The same kind of reaction takes place with methyl and ethyl alcohols. Amyl nitrate, after exposure to light, yields after some time ethereal salts of valeric acid, having a very agreeable odour. On pouring ethyl alcohol over uranium acetate, acetaldehyde, acetic acid, and ethyl acetate are formed. Uranium acetate, treated in the same manner with amyl alcohol, yields amyl acetate and ethyl valerate. B. B.

Action of Chlorine on Tetramethylethylene. By A. CHOUPOTSKY and N. MARIUTZA (*J. Russ. Chem. Soc.*, **21**, 431—434).—Tetramethylethylene was obtained by synthesis from isobutyric chloride and zinc methyl. This hydrocarbon, when subjected to the action of chlorine at the ordinary temperature, yielded the monochlorotetramethylethylene, $C_6H_{11}Cl$, which was purified by fractional distillation. On heating it with water in sealed tubes, it was found that it gradually disappeared, and at last *dimethyl isopropenyl carbinol*, $C_6H_{12}O$, was obtained as an aromatic liquid of sp. gr. 0·8560 (at 0°), and 0·8416 (at 19·5°). It boils at 117·5—118°, and yields an acetate and a

dibromide. Etherification with acetic acid (Menshutkin's method) confirms the view that it is a tertiary alcohol, $CMe_2(OH){\cdot}CMe{:}CH_2$.

B. B.

Action of Acids on Dimethyl Isopropenyl Carbinol. By N. MARIUTZA (*J. Russ. Chem. Soc.*, **21**, 434—436).—Dimethyl isopropenyl carbinol (see foregoing abstract) was subjected to the action of sulphuric and hydrochloric acids. When it was heated at 100° with dilute sulphuric acid (containing 1 per cent. or more), the product was a viscid oil, boiling above 100°, seemingly the product of condensation of a hydrocarbon formed by the action of very dilute acids.

After heating for 20 to 30 minutes in a water-bath with hydrochloric acid of 0·1 per cent., a very mobile liquid hydrocarbon, boiling at 68—69°, was obtained. It yields two additive products with bromine, the lower one containing less bromine being formed at a low temperature, the higher one after a longer time, or on gently warming; the latter has the formula $C_6H_{10}Br_4$. The hydrocarbon is C_6H_{10}, and as it is produced by the removal of one molecule of water from an alcohol of the above constitution, its formula can be only $CH_2{:}CMe{\cdot}CMe{:}CH_2$, *diisopropenyl*.

B. B.

Derivatives of Heptamethylene. By MARKOWNIKOFF (*Compt. rend.*, **110**, 466—468).—Suberone, contrary to the statement of Spiegel, is easily reduced to the corresponding alcohol, $C_7H_{13}{\cdot}OH$, by the action of sodium in presence of alcohol. This *suberonyl alcohol* is a colourless, somewhat viscid liquid, with a mouldy odour different from that of suberone. It is insoluble in water, and boils at 184—185° under a pressure of 741 mm.; sp. gr. at 15° compared with water at the same temperature = 0·9595. It combines easily with phenylcarbimide to form *suberonyl phenylcarbamate*, $NHPh{\cdot}CO{\cdot}OC_7H_{13}$, which crystallises in long, colourless, quadrangular prisms melting at 85°.

Concentrated hydrochloric and hydriodic acids dissolve suberonyl alcohol, and if the solution is heated for some time and then diluted with water, suberonyl chloride or suberonyl iodide is precipitated. The former is lighter than water, and distils without decomposition; the latter is heavier than water, and decomposes when distilled.

Suberonyl iodide, when treated with alcoholic potash, yields *suberonylene*, C_7H_{12}, which has a strong odour, boils at 114·5°, and combines energetically with bromine to form a heavy liquid with an odour of terebenthene. A small quantity of suberonyl ethyl ether, $C_7H_3{\cdot}OEt$, is formed in the same reaction.

When suberonyl alcohol is heated at 230—250° with 7 vols. of hydriodic acid of sp. gr. 1·96, it yields *heptamethylene*, C_7H_{14}, which boils at 98—101°; sp. gr. at 0° = 0 7791. It is a colourless liquid with a feeble odour similar to that of pure benzene. It is not attacked by bromine in the cold, and is only slowly dissolved by sulphuric or nitric acid, or a mixture of the two. The hydrocarbons C_8H_{16} and C_9H_{18}, with the nucleus C_6H_{12}, readily combine with bromine in presence of traces of aluminium bromide. The boiling point and specific gravity of heptamethylene are almost identical with those of heptanaphthene (100—101° and 0·7788).

Suberoxime dissolves in hydrochloric acid, and is reprecipitated by an alkali, but redissolves in excess. It is easily reduced by sodium in alcoholic solution, and yields *amidoheptamethylene*, a viscid liquid with a strong odour resembling that of the volatile alkaloïds.

Suberone when reduced yields, in addition to the alcohol, a liquid of high boiling point, which is probably the corresponding pinacone.

These compounds are all regarded as derivatives of heptamethylene, $\begin{matrix} CH_2\cdot CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2\cdot CH_2 \end{matrix}\!\!>\!CH_2$.

C. H. B.

Pentatomic Alcohol and an Unsaturated Glycerol from Diallyl Carbinol. By W. Doubinevitch (*J. Russ. Chem. Soc.*, 21, 467—474).—The preparation of a pentatomic alcohol was attempted in vain by Saytzeff, by Dieff, and lastly by Reformatsky (see this vol., p. 353). Diallyl carbinol was suspended in water in a flask, and treated, with constant agitation, with a 1 per cent. solution of potassium permanganate. In order to prevent the decomposition of the products of reaction which takes place when the solution is heated, magnesium sulphate was added, and the neutral volatile products, consisting chiefly of unchanged diallyl carbinol, were distilled off. From the residue, manganese dioxide was separated by filtration, and the filtrate evaporated to dryness at 40—50°. The residue was then treated with alcohol of 96 per cent., and after the alcohol had been distilled off, the residue was extracted with ether containing 5 per cent. of alcohol, and the solution filtered. At last, after extracting the residue with pure ether forty times, and evaporating the ethereal solution, a thick, nearly colourless, extremely bitter liquid was obtained, soluble in water and alcohol, but only sparingly in ether. It boils at 203—204° under a pressure of 37 mm., and has a sp. gr. of 1·0923 at 17·5°. Its composition corresponds with the formula $C_7H_{11}(OH)_3$. With bromine, it yields a very unstable additive product, $C_7H_{11}O_3Br_2$, and the glycerol, on being treated with acetic anhydride at 165°, yields an acetate, $C_7H_{11}O_3Ac_3$, of sp. gr. 1·0862 at 0°. The above residue, after extraction of this trihydric glycerol with ether, was dissolved in water, acidified with 10 per cent. sulphuric acid, and repeatedly shaken with ether in order to remove organic acids; these were found to consist chiefly of formic acid; no other organic acids were isolated. After this, the sulphuric acid solution was neutralised with potash, and treated with a large amount of alcohol, in order to precipitate potassium and magnesium sulphates, and the filtrate after evaporation was again treated in the same way. From this solution, a thick, oily liquid was precipitated on adding ether; this was dissolved in alcohol, neutralised with alcoholic potash, the potassium salts removed by filtration, and finally the alcoholic solution was fractionally precipitated by ether. All the fractions were found to be homogeneous, and only the first contained a trace of mineral salts. After drying, the *pentatomic alcohol*, $C_7H_{11}(OH)_5$, was obtained as a viscous mass of an agreeably sweet taste, closely resembling that of glucose. It could not be obtained in the crystalline state. It is soluble in water and alcohol, but quite insoluble in ether, differing in this respect from its first anhydride obtained by Dieff (*loc. cit.*). On heating it at 170°

with acetic anhydride and some acetic acid, used as a solvent, the *pentacetate*, $C_7H_{11}O_5Ac_5$, was obtained as a thick liquid, almost insoluble in water. The pentabenzoate could not be obtained in the pure state. The oxidation of diallyl carbinol takes place in two phases: at first only one double link of the carbinol is attacked, and the triatomic alcohol, $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH{:}CH_2$, is formed; then the elements of hydrogen dioxide are again taken up with the production of the pentatomic alcohol,

$$OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH.$$

The author proposes to investigate the process of dehydration of the pentatomic alcohol in order to ascertain why in Reformatsky's and Saytzeff's experiments its first anhydride was obtained instead of it.

B. B.

Derivatives of Erythrol. By E. GRIMAUX and C. CLOEZ (*Compt. rend.*, **110**, 462—465).—Hydrofurfurane bromide, obtained by Henninger's method, was heated in sealed tubes with fuming hydrobromic acid at 110° for six hours. The solid product is erythrene tetrabromide, and may be recrystallised from alcohol.

Erythrane, prepared by Henninger's method, yields hydrofurfurane when heated with 2·5 parts of glacial formic acid. This result shows that hydrofurfurane is not derived from erythrene, but from its anhydride erythrane, which behaves as a dihydric alcohol.

If bromine dissolved in chloroform is added to a chloroform solution of erythrol, and the mixture is allowed to evaporate spontaneously, erythrol bromide, $CH_2Br{\cdot}CHBr{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, is obtained in hard, bulky, hexagonal tables which melt at 81—82° and are very soluble in alcohol, ether, and chloroform.

Another bromhydrin was obtained by Champion, by the action of hydrobromic acid on erythrol. The authors obtained the same compound, $CH_2Br{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2Br$, by heating erythrol with ten times its weight of fuming hydrobromic acid at 100° for 120 hours, or at 120° for 18 hours. It crystallises from chloroform in small, nacreous tables which melt at 135°. Erythrene tetrabromide melting at 114° is also formed at the same time.

From these results the authors conclude that the compounds obtained by the reduction of erythrol have the following constitutions:—

$$O<\begin{matrix}CH_2{\cdot}CH{\cdot}OH\\ \quad\ \ |\\ CH_2{\cdot}CH{\cdot}OH\end{matrix}. \qquad\qquad O<\begin{matrix}CH_2CH\\ \quad\ \ \|\\ CH_2CH\end{matrix}.$$

Erythrane. Hydrofurfurane.

$$CH_2{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}OH. \qquad\qquad CH_2{:}CH{\cdot}CH{:}CH_2.$$

Dehydr-erythrol. Erythrene.

C. H. B.

Benzoic Acetals of Sorbite. By J. MEUNIER (*Compt. rend.*, **110**, 577—580).—The monobenzoic acetal, or *monobenzylal sorbite*, $C_6H_{13}O_5Bz$, is obtained by mixing a solution of sorbite in its own weight of water with the requisite volume of benzaldehyde, and one-tenth its volume of hydrochloric acid of 22° B. A large proportion

crystallises from the liquid and a further quantity is obtained by neutralising the mother-liquor with sodium carbonate. It is purified by recrystallisation from warm alcohol or warm water. It crystallises from water in transparent, highly refractive, rectangular prisms, which melt without decomposition at 163—164° if heated slowly, or at 172—175° if heated rapidly. From alcohol, in which it is less soluble than in water, it separates in smaller crystals. When boiled with very dilute acids, the acetal is decomposed with liberation of benzaldehyde.

Dibenzylal sorbite, $C_6H_{12}O_5Bz_2$, is obtained by mixing a concentrated solution of sorbite with its own volume of hydrochloric or sulphuric acid, and adding benzaldehyde. A white, amorphous solid, insoluble in water, is obtained and was previously described as the dibenzoic acetal (Abstr., 1889, 479). It is, however, a mixture of two substances, one of which dissolves in 1000 parts of boiling water and gelatinises on cooling, whilst the other is quite insoluble in hot water and has exactly the composition of dibenzylal sorbite.

The dibenzoic derivative melts at 162°, is insoluble in water containing sulphuric acid, and is not decomposed when boiled with it.

The product which dissolves in hot water, on the other hand, is completely decomposed in presence of minute quantities of hydrochloric and sulphuric acids. The gelatinised mass can be freed from water by filtration and pressure. The product melts at about 200°, but has no definite melting point; dissolves in acetic acid, benzene, chloroform, and especially ether, from which it gelatinises; and contains about 2 per cent. less carbon than dibenzylal sorbite.

C. H. B.

Formation of Volatile Fatty Acids from Dextrose. By O. LOEW (*Ber.*, **23**, 865—866).—When air-dried platinum-black, prepared by the method lately described (this vol., p. 453), is placed in dilute solutions of dextrose, a rancid odour soon becomes noticeable and increases in intensity for two days; on warming the fresh mixture at 60—70°, the smell is stronger and becomes noticeable even more quickly. This action takes place even in presence of an antiseptic such as benzoic acid, so that it cannot be due to a ferment.

Levulose and lactic acid do not behave like dextrose in this respect; the slight odour observed resembles rather that of formic acid.

No odour is observed when freshly prepared platinum-black which has not been exposed to the air, or when platinum-black which has been used before is employed; the smell is observed, however, when this inactive black is treated with hydrogen peroxide, or dried in the air and then placed in the solution of dextrose. If the dextrose solution is boiled with the active black and a little calcium carbonate, the concentrated, filtered solution gives off no rancid odour on treatment with sulphuric acid, probably because the occluded oxygen is so quickly used up in converting the dextrose into gluconic acid, or some similar compound, that the other reaction cannot take place.

When cane-sugar is treated with active platinum-black, the rancid odour is not observed, but inverted sugar yields traces of formic acid, and a disagreeably smelling acid which, from an analysis of its silver

salt, is probably valeric acid, although it may be a mixture of several acids. F. S. K.

Action of Ethyl Acetoacetate on Dextrose in presence of Alcoholic Ammonia. By P. Biginelli (*Gazzetta*, **19**, 215—217).—When a solution of dextrose (10 grams) in 75 per cent. alcohol (35 grams), ethyl acetoacetate (15 grams), and a solution of ammonia (1 gram) in 94 per cent. alcohol are mixed and left for one or two days, a granular deposit is formed consisting of a mixture of dextrose and a compound of dextrose and ammonia; later on, another substance separates, which after repeated crystallisation may be obtained in silky, white needles; these melt at 189—190°, and have the composition, $C_{16}H_{20}O_8N$. This substance dissolves sparingly in cold water and in alcohol, and is almost insoluble in ether and chloroform; it has a feeble reducing action on Fehling's solution. Both the aqueous and alcoholic solutions have a neutral reaction; the former is coloured red by a solution of ferric chloride. It dissolves in acids, and in both aqueous and alcoholic potash. When suspended in alcohol, it is not affected by a current of nitrous acid.

If the mixture of dextrose, &c., mentioned above is heated in closed tubes at 100—110°, groups of acicular crystal, are formed which melt at 130—131°, and have the composition $C_{10}H_{16}NO_5$.

This preliminary note is published by the author in order to reserve the right of further investigation in this field. S. B. A. A.

Pentacetyllevulose. By E. Erwig and W. Koenigs (*Ber.*, **23**, 672—675; compare Abstr., 1889, 952, 1431).—*Pentacetyllevulose*, $C_6H_7O(OAc)_5$, can be prepared by dissolving levulose (3 grams) in warm glacial acetic acid (3 c.c.), gradually adding the solution to almost boiling acetic anhydride (9 c.c.) containing 0·1 to 0·2 gram of zinc chloride, and then boiling for five minutes to complete the reaction. The yield is about 66 per cent. of the levulose employed. It is a soft, colourless, hygroscopic resin, readily soluble in alcohol, ether, chloroform, benzene, and glacial acetic acid, but only sparingly in light petroleum and carbon bisulphide; it is soluble in, and partially decomposed by boiling water, and its solution in chloroform is feebly dextro-rotatory. When boiled for two hours with decinormal sulphuric acid diluted with an equal volume of water, it is completely decomposed, levulose being regenerated. It reduces Fehling's solution on boiling, and is completely decomposed when boiled with potassium dichromate and glacial acetic acid. It does not combine with phenylhydrazine. F. S. K.

Extraction of Raffinose from Molasses: Separation of Raffinose from Saccharose. By L. Lindet (*Compt. rend.*, **110**, 795—798).—The molasses is diluted with five or six times its weight of cold water and agitated with mercuric sulphate, which precipitates the impurities The liquid is filtered, treated with bartyta to neutralise the sulphuric acid resnlting from the decomposition of the mercuric sulphate, boiled, and concentrated in a vacuum. The syrup

is dissolved in methyl alcohol, which precipitates a further quantity of impurities.

One hundred parts of methyl alcohol dissolve 9·5 parts of raffinose and 0·4 part of saccharose. The solubility of saccharose increases as the alcohol is more and more hydrated. One hundred parts of ethyl alcohol of 95° dissolve only six parts of raffinose. The solubility of saccharose in ethyl alcohol increases with the degree of hydration, but that of raffinose remains almost constant. The following table gives the quantities of raffinose and saccharose dissolved by 100 parts of alcohol of different strengths:—

	95°.	90°.	83°.	80°.
Saccharose	0·30	1·00	2·23	6·20
Raffinose............	0·06	0·08	0·10	0·21

The methyl alcohol solution of the syrup is dehydrated at its boiling point by means of lime, the raffinose is precipitated by the addition of ordinary alcohol, and the product is recrystallised from ethyl alcohol of 80—85°. C. H. B.

Melezitose. By A. Alechin (*J. Russ. Chem. Soc.*, **21**, 407—421). —Berthelot and Villiers have studied this carbohydrate and attributed to it the formula $C_{12}H_{22}O_{11} + H_2O$. The author has prepared melezitose from Persian manna, called terenjabin, a product of *Alhagi Maurorum* (D.C.) Terenjabin containing about 38 per cent. of melezitose was dissolved in 4 parts of warm water and the impurities removed by decantation. The clear solution was then evaporated to half its bulk on a water-bath and allowed to remain for 3 to 4 days, when the melezitose separates out completely in the crystalline state. It was purified by dissolving it in hot water, adding an equal volume of strong alcohol, and filtering the boiling solution; on cooling, the melezitose separates and is again recrystallised. The formula of the crystals, which are rhombic prisms, is $C_{18}H_{32}O_{16} + 2H_2O$; they become opaque on exposure to the air and lose their water at 110°; when anhydrous, they melt at 147—148°. Anhydrous melezitose is also obtained by precipitating the hot aqueous solution with strong alcohol. Its sp. gr. at 17°/4° is 1·540. It is less soluble in water than saccharose, 100 parts at 17° containing 26·8 parts of anhydrous melezitose, and 75·6 parts at 100°. The spec. rotatory power of the anhydrous melezitose $[\alpha]_D = + 87·72° + 0·074p$, that of the hydrated compound $[\alpha]_D = +83° + 0·07014p$ (p = percentage in 100 parts of the solution). For an imaginary 100 per cent. solution $[\alpha]_D = + 95° 12'$. Melezitose, on inversion with dilute mineral acids, yields at first *turanose* and dextrose; the former is a new saccharose of the formula $C_{12}H_{22}O_{11}$ with $[\alpha]_D = +$ 65° to 68°; it is insoluble in alcohol, by which it is separated from its solution, and melts at 65—70°. On long continued action of the acid, dextrose alone is obtained. Pure melezitose does not itself ferment when submitted to the action of ferments or diastase, but only the products of its inversion. The phenylhydrazine-derivative of melezitose is an unstable compound melting at 172°. The acetyl-derivative, $C_{18}H_{21}O_{16}Ac_{11}$, forms rhombic prisms of sp. gr. =

1·32 at 0°/4°, melting at 117° with $\alpha[D] = +110·44°$. Several determinations of the molecular weight of melezitose by Raoult's method confirm the formula $C_{18}H_{32}O_{16}+2H_2O$; by the same method the molecular formula of the undecacetyl-derivative is confirmed, but for the new "turanose" results were obtained corresponding with the formula $C_6H_{12}O_6$, although its sodium-derivative is $C_{12}H_{21}O_{11}Na$.

B. B.

Callose, a new Fundamental Substance in Vegetable Membrane. By L. MANGIN (*Compt. rend.*, **110**, 644—647).—Callose occurs in various organs of a very large number of plants and is especially important in the thallophytes, but was not found in certain Uredineæ. Its existence is often difficult to prove owing to its admixture with other substances and its resistance to the action of solvents.

The callose was not isolated sufficiently pure for analysis. It is distinguished from cellulose by its insolubility in Schweizer's reagent even after the action of acids, and by the yellow coloration which it gives with iodophosphoric acid. From pectic compounds, it is distinguished by its insolubility in ammonia, and alkaline carbonates in the cold, and its different behaviour with colouring matters. It is colourless, amorphous, insoluble in water and alcohol, but dissolves readily in sodium or potassium hydroxide of 1 per cent., and is also soluble in concentrated sulphuric acid and concentrated solutions of calcium chloride and stannous chloride. It does not dissolve in cold solutions of alkaline carbonates or ammonia, but swells up and gelatinises. With various staining fluids, callose gives reactions which serve to distinguish it from other substances in the vegetable membrane. With iodine it acquires a yellow coloration. C. H. B.

Preparation of Hydrazine from Aldehyde-ammonia. By T. CURTIUS and R. JAY (*Ber.*, **23**, 740—752).—It has previously been observed by Curtius (*Diazoverb. der Fettreihe*, Munich, 1886) that aldehyde-ammonia, when treated with nitrous acid in acid solution, yields an oily nitrosamine, which is volatile in a current of steam and may be distilled in a vacuum without decomposition. From the analysis and vapour-density of the substance, the conclusion was drawn that it contained 3 mols. of aldehyde and 2 atoms of nitrogen. The condensation of 3 mols. of ethyl diazoacetate to form triazoacetic acid, investigated by the authors (Abstr., 1889, 393), has led them to examine this nitrosamine further, in the hope of obtaining hydrazine from it more readily than by the previous methods. They find that hydrazine can be formed in the manner shown below, but the yield is so small that this reaction cannot be employed as a method for its preparation.

When a solution of sodium nitrite is added to a well-cooled solution of aldehyde-ammonia in dilute sulphuric acid, the nitrosamine separates and may be extracted with ether, the aqueous solution being then several times treated with small quantities of sodium nitrite and sulphuric acid, and extracted after each treatment with ether. The combined extracts are shaken with a solution of sodium carbonate and with water, and finally with solid potassium carbonate,

the ether evaporated, and the residual oil distilled in a current of steam. The oil thus obtained, on analysis, gave numbers agreeing with the formula $C_6H_{12}N_2O_3$, which was confirmed by a determination of its vapour-density. It is a lemon-yellow liquid, which has a camphor-like odour, and boils at 95° under 35 mm. pressure without decomposition. It is insoluble in water, but miscible with alcohol, ether, chloroform, and benzene. It gives Liebermann's reaction for nitroso-compounds, and is converted by hot dilute sulphuric acid into paraldehyde, and must therefore be a nitroso-derivative of an imido-paraldehyde or *paraldimine*, its constitution being represented by the formula

$$C_5H_{11}O_2{\cdot}CH{:}N{\cdot}NO.$$

When hydrogen chloride is passed into a moist ethereal solution of nitrosoparaldimine, a white, crystalline precipitate of *paraldimine hydrochloride*, $C_5H_{11}O_2{\cdot}CH{:}NH,HCl$, separates; this crystallises in small, anisotropic, colourless needles, which are unaltered in dry air, and blacken on heating. On remaining in moist air, they pass without change of form into ammonium chloride. They are insoluble in ether, chloroform, and benzene, but are readily taken up by water and absolute alcohol, which at once convert them into paraldehyde and ammonium chloride; this decomposition is brought about still more readily by the action of acids. Nitrous acid converts it into a nitrosamine identical with the compound obtained from aldehyde-ammonia.

By the action of silver oxide on paraldimine hydrochloride suspended in dry ether, free *paraldimine*, $C_5H_{11}O_2{\cdot}CH{:}NH$, is obtained as a mobile, colourless liquid boiling at 140° almost without decomposition, and solidifying in a freezing mixture. Its vapour-density was found to be 4·451, corresponding with a molecular weight of 128·5. On remaining in a sealed tube for a few weeks, it passes into a solid, glassy mass, which has the same percentage composition. The liquid readily loses ammonia in presence of water or alcohol, forming paraldehyde.

Amidoparaldimine or *paraldylhydrazine*, $C_5H_{11}O_2{\cdot}CH{:}N{\cdot}NH_2$, is prepared by treating an ethereal solution of nitrosoparaldimine with zinc-dust and acetic acid. After the addition of alkali, the solution is extracted with ether, the ethereal extract dried over barium oxide, and evaporated in a vacuum. The free base is not volatile without decomposition, and could not be obtained pure. When hydrogen chloride is passed through the dry ethereal solution, the *hydrochloride* separates in needles, which are exceptionally hygroscopic. Both of these compounds are decomposed by boiling dilute sulphuric acid, with formation of hydrazine sulphate, but, as already mentioned, the yield is very small. It may also be obtained directly from nitrosoparaldimine by treating the latter with dilute sulphuric acid and zinc-dust until the oil has disappeared, quickly filtering, and boiling vigorously for a few minutes.

The small yield of hydrazine obtained is probably due to the fact that in the reduction of the nitroso-compound the reaction does not stop with the formation of paraldimine, but goes further with formation of the compound $C_5H_{11}O_2{\cdot}CH_2{\cdot}NH{\cdot}NH_2$, and that this compound,

like diethylhydrazine, does not lose the hydrazine-group by the action of acids. H. G. C.

Constitution of Citrazinamide. By S. RUHEMANN (*Ber.*, **23**, 831—832).—A reply to Lovén (*Ber.*, **22**, 3053), defending the formula proposed by the author for citrazinamide.

Chlor- and Hydroxy-acids of the Fatty Series. By P. MELIKOFF and PETRENKO-KRITTCHENKO (*J. Russ. Chem. Soc.*, **21**, 393—397). —The authors have studied the behaviour of α-hydroxy-β-halogen-lactic acids and the corresponding butyric acids on distillation with water, and show that carbonic anhydride, hydrogen chloride, and an aldehyde or ketone containing one atom of carbon less than the original acid are obtained. The sodium salt of the first acid yields acetaldehyde, that of the second, propaldehyde. Chlorhydroxyisobutyric acid, under the same conditions, yields dimethyl ketone, and it is therefore a β-halogen-α-hydroxy-acid. The same is the case as regards the chlorhydroxyvaleric acid, melting at 75°, obtained from tiglic and hydrochloric acids, as it yields ethyl methyl ketone. The formation of ethyl methyl ketone confirms the generally adopted formula of tiglic acid, CHMe:CMe·COOH. B. B.

Action of Methyl Diazoacetate on the Ethereal Salts of Unsaturated Acids. By E. BUCHNER (*Ber.*, **23**, 701—707).—Methyl diazoacetate combines with methyl acrylate in the same manner as with methyl fumarate and cinnamate (Abstr., 1888, 1274), forming a well-crystallised additive compound, $C_3H_4N_2(COOMe)_2$, which, on heating for 40 minutes at 160—185°, loses all its nitrogen and yields an oil boiling between 205° and 215° (718 mm.) and having the composition $C_7H_{10}O_4$. The vapour-density of 155 agrees with this formula, but the further examination showed that the oil is a mixture of the methyl salts of two isomeric acids which may be separated by their different solubilities in water or ether. The acid which is less soluble in water crystallises from that liquid in compact forms, probably belonging to the rhombic system, melts at 175°, and distils without decomposition. It has the composition $C_5H_6O_4$, and is not acted on by alkaline potassium permanganate and sodium amalgam, and appears, therefore, to be a *trimethylenedicarboxylic acid*, in which, from its mode of formation, the carboxyl-groups must be attached to different carbon-atoms. A trimethylenedicarboxylic acid (1·2) has been previously prepared by Conrad and Guthzeit (Abstr., 1884, 992), but as this melts at 139°, and readily passes into the anhydride on distillation, it cannot be identical with the acid above described. This has also been confirmed by a direct comparison of the two acids. The author has also shown that Conrad and Guthzeit's acid is unacted on by alkaline potassium permanganate or sodium amalgam, and has confirmed the similar results obtained by Fittig and Roeder (*Annalen*, **227**, 18) and by W. H. Perkin, jun. (Trans., 1885, 812) for trimethylenedicarboxylic acid (1·1).

The existence of two trimethylenedicarboxylic acids (1·2) can readily be explained by Baeyer's extension of Van't Hoff's hypothesis

to compounds having a closed chain of atoms (Abstr., 1888, 1071). Two forms should theoretically exist, in one of which (the Γ-*cis* or maleïnoïd form) the carboxyl-groups lie on the same side of the ring, whilst in the other (the Γ-*cistrans* or fumaroïd form) they lie on opposite sides. As Conrad and Guthzeit's acid readily yields an anhydride, it probably represents the Γ-*cis* modification, whilst the acid described in this paper, which at most forms an anhydride only with difficulty, must be the Γ-*cistrans* acid.

The latter may also be crystallised from ether, from which it separates in white aggregates of needles, the aqueous solution of which gives a slight brown coloration with ferric chloride. The *zinc* salt is much more readily soluble in cold than in hot water, and on heating the solution separates in nodular aggregates of microscopic crystals. The *silver* salt is sparingly soluble even in boiling water; on heating, it yields a colourless, crystalline sublimate, possibly consisting of the anhydride.

The second acid, which is more soluble in water than the foregoing, but less soluble in ether, forms fascicular groups of seemingly monoclinic needles, and melts at 138°. On boiling it with acetic chloride, it yields an anhydride which melts at 86—87°, and decomposes completely at 130°. The *zinc* salt, like that of the foregoing acid, is less soluble in hot than in cold water, whilst the *lead* and *silver* salts form crystalline precipitates. The acid reduces alkaline potassium permanganate immediately, and on reduction with sodium amalgam yields glutaric acid, which was identified by its analysis, melting point, and characteristic zinc salt. The acid under discussion must therefore be a *glutaconic acid*, and is probably identical with the one described by Conrad and Guthzeit as melting at 132—133°. H. G. C.

Molecular Weights of some Acids of the Oleïc Series. By O. Šulc (*Listy Chem.*, **13**, 201—203).—The author finds that the lowering of the freezing point, as obtained by Raoult's method, for crotonic, chlorocrotonic, and chlorisocrotonic acids, in acetic acid solution, corresponds with a simple molecule. An aqueous solution of crotonic acid indicates again a simple molecule, whereas a solution of the same acid in benzene points to a double molecular weight, $(C_4H_6O_2)_2$. B. B.

Acids Poor in Carbon obtained from Baku Petroleum. By O. Aschan (*Ber.*, **23**, 867—875).—The alkaline solution obtained as a bye-product in the purification of Baku petroleum contains water, hydrocarbons, and a mixture of various acids; when the crude acid mixture (100 kilos.) obtained therefrom is distilled, a small portion passes over between 220° and 270°. This fraction can be freed from hydrocarbons by dissolving it in 5 per cent. soda, acidifying the clear solution with dilute sulphuric acid, and extracting the precipitated oils with ether; the yield of this product is about 6 kilos.

Methyl hexamethylenecarboxylate, $C_6H_{11}\cdot COOMe$, can be prepared from this mixture of acids by treating it with methyl alcohol and concentrated sulphuric acid, and repeatedly fractionating the methyl salts thus produced; in this way 105 grams of the pure methyl salt

was obtained. It is a colourless oil of sp. gr. 0·90547 at 18·4°, boils at 165·5—167·5° corr. (thermometer entirely in the vapour), and has an agreeable, fruity odour, which is, however, at the same time, somewhat nauseous. The free *acid*, $C_6H_{11}\cdot COOH$, obtained by hydrolysing the methyl salt with alcoholic potash, is a thick, colourless, disagreeably smelling oil of sp. gr. 0·95025 at 18·4°. It is not acted on by bromine at the ordinary temperature, but, on heating, evolution of hydrogen bromide commences; it is only slowly oxidised by nitric acid of sp. gr. 1·3, and very slowly by potassium permanganate in cold sodium carbonate solution. It decomposes calcium chloride with evolution of hydrochloric acid, and its barium and calcium salts are not decomposed by carbonic anhydride. It dissolves freely in concentrated sulphuric acid, but, on warming, decomposition sets in; it is gradually decomposed by phosphoric anhydride at the ordinary temperature. The *potassium* salt, $C_6H_{11}\cdot COOK$, is very readily soluble in water and alcohol, and is very hygroscopic. The *sodium* salt, $C_6H_{11}\cdot COONa$, separates from alcohol in ill-defined, hygroscopic prisms. The *calcium* salt, $(C_6H_{11}\cdot COO)_2Ca + 4H_2O$, separates in needles when its aqueous solution is evaporated over sulphuric acid; it loses its water completely on exposure to the air and is readily soluble in water and alcohol. When a concentrated aqueous solution is heated, the salt separates as a semi-solid, amorphous mass which becomes hard and granular when dried. The *barium* salt, $(C_6H_{11}\cdot COO)_2Ba$, is very readily soluble in alcohol, but more sparingly in water. When the acid is dissolved in baryta-water, the excess of barium hydrate precipitated with carbonic anhydride, and the filtered solution concentrated on the water-bath, it solidifies to a mass of anhydrous plates, which retain their crystalline form if they are quickly separated from the mother liquors; if, however, the crystals are allowed to remain in the solution, they deliquesce to a syrup on cooling, and on drying there remains a vitreous, amorphous mass which becomes crystalline when heated on the water-bath; the amorphous salt is also formed when aqueous solutions are evaporated at the ordinary temperature. The *silver* salt, $C_6H_{11}\cdot COOAg$, is moderately easily soluble in hot water. The *cadmium* salt, $(C_6H_{11}\cdot COO)_2Cd$, crystallises in anhydrous, nacreous plates, and is only sparingly soluble in cold water. The *chloride*, $C_6H_{11}\cdot COCl$, prepared by treating the acid with phosphoric chloride, boils at 167—169°, and is only very slowly decomposed by water. The *amide*, $C_6H_{11}\cdot CONH_2$, obtained by treating the chloride with dry ammonium carbonate, crystallises from water in nacreous plates, melts at 123·5°, and is moderately easily soluble in water and very readily in the other ordinary solvents; it dissolves freely in concentrated sulphuric acid, but is reprecipitated in crystals on the addition of water. The *anilide*, prepared from the chloride, separates from alcohol and from a mixture of benzene and light petroleum in slender needles melting at 93—94°.

The acid $C_8H_{14}O_2$ (b. p. 237—239°) and the acid $C_9H_{16}O_2$ (b. p. 251—253°), described by Markownikoff, have also been obtained in a pure condition from the mixture of acids referred to above.

F. S. K.

Glycollic Nitrile: Direct Synthesis of Glycollic Acid. By L. Henry (*Compt. rend.*, **110**, 759—760).—Formaldehyde and hydrocyanic acid in aqueous solution combine completely with development of heat and formation of glycollic nitrile, $CN\cdot CH_2\cdot OH$. The liquid is evaporated at a gentle heat and extracted with ether. Glycollic nitrile is a colourless, limpid, odourless liquid, with a peculiar, sweetish taste; it is very soluble in water, alcohol, and ether, but is insoluble in carbon bisulphide, chloroform, and benzene. At $-72°$ it solidifies to a crystalline mass, and the temperature rises to $-67°$; it boils with partial decomposition at 183° under a pressure of 759 mm., but if completely dried, it boils without change at 119° under a pressure of 24 mm.; sp. gr. at 12° = 1·100.

A minute quantity of potassium carbonate converts the nitrile into a brownish, crystalline mass which has not yet been examined; acetic chloride acts energetically and destructively; acetic anhydride acts energetically with great development of heat, and yields the acetate, $CN\cdot CH_2\cdot OAc$, which boils at 177°. Dilute acids rapidly convert the nitrile into glycollic acid with great development of heat.

C. H. B.

Hydroxytetric Acid. By C. Cloez (*Compt. rend.*, **110**, 583—586). —Demarçay obtained tetric and hydroxy-tetric acids by the action of alcoholic potash on the product of the action of bromine on ethyl methylacetoacetate. The author adopted Demarçay's method, except that, since no carbonic anhydride was evolved and the formation of dibromacetone was improbable, the product of the action of bromine on the ethyl methylacetoacetate was washed with water as soon as the colour of the bromine had disappeared. The ethyl dibromomethylacetoacetate was added gradually to alcoholic potash cooled by means of water, and the liquid, after dilution with water, was concentrated until all alcohol was expelled, strongly acidified with sulphuric acid, and exhausted with ether. When the ether is distilled off, hydroxytetric acid is obtained. Potassium hydroxide in methyl alcohol, aqueous potash, or even baryta-water, can be substituted for alcoholic potash. If ethyl dibromomethylacetoacetate is boiled with water, it readily saponifies, but the products contain a large proportion of black, insoluble substances. The same result is obtained even in presence of barium carbonate.

Hydroxytetric acid has the composition $C_5H_6O_4$, and after treatment with animal charcoal, crystallises from hot water in colourless crystals melting at 201—202°.

Ethyl hydroxytetrate, $C_5H_5O_4Et$, is obtained by the action of water on ethyl dibromomethylacetoacetate in presence of barium chloride, and is extracted by treatment with chloroform, from which it separates in colourless prisms which melt at 67—68°, and have a distinctly acid reaction. The silver ethyl salt crystallises in slender, colourless needles somewhat soluble in cold water, and but slightly altered when exposed to light. When treated with potassium hydroxide, the ethereal salt is decomposed, and on acidification with sulphuric acid, hydroxytetric acid is obtained.

If a solution of hydroxytetric acid in dilute alcohol is treated with gaseous hydrogen chloride, a colourless, neutral liquid is obtained

which boils at 224—226°, and has the composition of a diethyl-derivative of hydroxytetric acid. C. H. B.

Potassium Hydrogen Malonate, Quadromalonate, and Quadroxalate. By G. MASSOL (*Compt. rend.*, **110**, 793—795).—*Potassium hydrogen malonate*, $C_3H_3KO_4 + \frac{1}{2}H_2O$, crystallises in large, non-deliquescent, monoclinic prisms which lose their water of crystallisation at 120—130°, and decompose at a higher temperature with evolution of acetic acid; heat of dissolution of the anhydrous salt = − 5·11 Cal.; heat of dissolution of the hydrated salt = − 9·58 Cal.; heat of hydration ($\frac{1}{2}H_2O$) + 3·755 Cal. in the solid condition; heat of neutralisation of solid malonic acid by one equivalent of solid potassium hydroxide + 27·87 Cal.

Potassium quadromalonate, formed by the direct combination of the acid with the preceding salt, crystallises in large, brilliant, anhydrous prisms; heat of dissolution −13·52 Cal. The combination of the dissolved acid with the dissolved hydrogen-salt to form the dissolved quadromalonate develops +0·10 Cal.

Potassium quadroxalate crystallises with 4 mols. H_2O, which are expelled at 110°; heat of dissolution of the hydrated salt −17·94 Cal.; of the anhydrous salt −12·79 Cal. The combination in solution of the hydrogen salt with the free acid to form the quadroxalate develops +0·05 Cal.; the combination of the solid salt and acid to form the solid quadroxalate would develop +0·95 Cal.; heat of hydration of the solid quadroxalate +2·29 Cal.

The heats of formation of all the potassium malonates are distinctly lower than those of the corresponding oxalates. C. H. B.

Symmetrical Diethylsuccinic and Methylethylsuccinic Acids. By BUITCHICHIN and ZELINSKY (*J. Russ. Chem. Soc.*, **21**, 376—389).—In a former paper (Abstr., 1889, 377), the authors have shown that two diethylsuccinic acids may be obtained from the product of the action of potassium cyanide on ethyl α-bromobutyrate. The symmetrical ethyl cyanodiethylsuccinate is not so easily acted on by hydrochloric acid as the corresponding dimethyl-compound, and the hydrolysis therefore was effected by means of alcoholic potash. The potassium diethylethenyltricarboxylate thus formed was decomposed with weak hydrochloric acid, and the liberated acids extracted with ether. In this way, a mixture of the two isomeric diethylsuccinic acids was obtained, and the acids separated by recrystallisation, taking advantage of the difference in their solubility. The sparingly soluble acid melts at 190—191°, and is the "fumaroïd" form, whereas the easily soluble "maleïnoïd" acid melts at 127—128°. These two acids are identical with those obtained by Bischoff and Hjelt (Abstr., 1888, 1057) from ethyl malonate by synthesis. On heating, both acids behave in a manner analogous to the dimethylsuccinic acids (compare Abstr., 1889, 692). They both yield the same anhydride, an oily liquid boiling between 244° and 246°. On adding water, the anhydride obtained from either of the two acids gives a mixture of much "maleïnoïd" acid (m. p. 127—128°) with a very small quantity of the "fumaroïd" acid (m. p. 190—191°). It is impossible

to convert one acid into the other by boiling with water or weak hydrochloric acid, except under pressure, as found by Bischoff and Hjelt. The *ethyl salts*, prepared from ethyl iodide, and the corresponding silver salts are not identical, for although the "fumaroïd" compound boils at 235—239°, and the "maleïnoïd" at 237—239°, the sp. gr. of the first at 18° F. is 0·9736 and that of the second 0·9904, referred to water at 0°.

In a similar way, the ethylmethylsuccinic acids were prepared (*a*) by the action of ethyl sodiocyanopropionate on ethyl bromobutyrate, and (*b*) of ethyl sodiocyanobutyrate on ethyl bromopropionate. The ethyl α-cyanomethyl-β-ethylsuccinate obtained in (*a*) boils at 275—278°, its sp. gr. is 1·0542; the ethyl α-cyanethyl-β-methylsuccinate obtained in (*b*) boils at 283—285°, and its sp. gr. is 1·0172. Both ethyl salts were hydrolysed by hydrochloric acid, and in each case a mixture of two acids melting at 169—170° and at 84—85° was obtained. The ethereal salt boiling at 283—285° yields a larger proportion of the acid melting at 84—85°, that boiling at 275—278° yields a larger proportion of the acid melting at 169—170°. The "fumaroïd" acid is more sparingly soluble in water than the "maleïnoïd" acid. The calcium salt of the "fumaroïd" acid contains $5H_2O$, that of the "maleïnoïd" acid $1H_2O$, and the corresponding barium salts contain $2H_2O$ ("fumaroïd") and $5H_2O$ ("maleïnoïd"). At a higher temperature, both acids yield one and the same anhydride, boiling at 244—245°, which, on addition of water, yields chiefly the "maleïnoïd" acid (m. p. 84—85°) with only a small admixture of the "fumaroïd" acid (m. p. 169—170°). Here again, as in the case of diethylsuccinic and dimethylsuccinic acids, there is a possibility of passing over from the acid with a higher melting point—"fumaroïd"—into the "maleïnoïd" acid of lower melting point, so that the anhydrides exist only for the "maleïnoïd" form. All "maleïnoïd" forms of the disubstituted succinic acids give off the elements of water at a lower temperature than the corresponding "fumaroïd" isomerides.

B. B.

Theory of Anhydride Formation in the case of Acids of the Succinic Series. By C. A. Bischoff (*Ber.*, **23**, 620—623).—The author has studied the behaviour of a large number of acids of the succinic series with the view of ascertaining what conditions determine the formation of an anhydride, more especially with regard to the influence of alkyl-groups (compare Auwers and Meyer, this vol., p. 479).

The fact that pyrocinchonic acid and xeronic acid cannot be obtained, whilst maleïc acid and fumaric acid are capable of existence, is best explained by assuming that, in the substitution of hydrogen by methyl- or ethyl-groups the carboxyl-groups are brought nearer together, probably because the doubly-bound carbon-atoms approach one another; the result of this may be that the space which would be occupied by the hydroxy-groups of the acid molecule, if the latter could exist, is no longer available, and anhydride formation results.

That the formation of an inner anhydride is also facilitated when an ethyl-group is substituted for a methyl-group is exemplified by the behaviour of levulinic acid and its homologues. Levulinic acid and

both α- and β-ethyllevulinic acid distil unchanged; α-ethyllevulinic acid, on the other hand, as has been shown by Thorne (Trans., 1887, 336) is slowly converted into a lactone on distillation. By assigning to these levulinic acids the constitution of γ-hydroxy-acids, it is seen that this difference in behaviour is analogous to that exhibited in the case of maleïc acid and its homologues.

The conclusion to be drawn from these considerations, is that anhydride formation takes place the more readily the larger the atomic complex which replaces the hydrogen; how far this conclusion is in accordance with experiment is shown in the paper on anhydride formation (this vol., p. 744).

The formation of imides and anil-derivatives, which has been especially studied in the case of the two symmetrical dimethylsuccinic acids, has been found to be influenced in an analogous manner.

F. S. K.

Preparation of Mono-, Di-, and Tri-substituted Succinic Acids from Ethyl Malonate. By C. A. Bischoff (*Ber.*, **23**, 631—633).—The method previously described for the preparation of succinic acid from ethyl malonate can be employed for the preparation of mono-, di-, and tri-substituted succinic acids. For this purpose, ethyl sodiomalonate is treated with the ethyl salt of a chloro- or bromo- mono- or di-substituted acetic acid, and the sodium-derivative of the product is treated with the iodide or chloride of an alcohol radicle, or the sodium-derivative of the ethyl salt of a substituted malonic acid is treated with the ethereal salt of a chloro- or bromo- mono- or di-substituted acetic acid. The identity of the ethereal salts obtained by these two methods was proved by measurements of their physical constants (compare this vol., p. 745).

The crude substituted ethyl ethenyltricarboxylate obtained by either of these two methods is fractionated, and each fraction heated with sulphuric acid (1 : 1) at 150—170° until the whole is soluble in alkali; the reaction which takes place consists essentially in the elimination of carbonic anhydride (1 mol.) and ethylene (3 mols.). The product is then freed from sulphuric acid, and the various acids obtained separated by fractional crystallisation. In the case of the benzyl-derivatives of ethyl ethenyltricarboxylate, alcoholic potash is employed instead of sulphuric acid, as they are only slowly hydrolysed when heated with sulphuric acid.

F. S. K.

Methylsuccinic, Ethylsuccinic, and Asymmetrical Dimethylsuccinic Acid. By C. A. Bischoff and A. v. Kuhlberg (*Ber.*, **23**, 634—638).—Ethyl ethenyltricarboxylate, $COOEt{\cdot}CH_2{\cdot}CH(COOEt)_2$, prepared from ethyl sodiomalonate and ethyl chloracetate, boils at 278·3° (corr.) and yields succinic acid on hydrolysis.

Ethyl propenyltricarboxylate, $COOEt{\cdot}CHMe{\cdot}CH(COOEt)_2$, prepared from ethyl sodiomalonate and ethyl α-bromopropionate, boils at 270·3° (corr.), and yields pyrotartaric acid on hydrolysis.

Ethyl methylethenyltricarboxylate, $COOEt{\cdot}CH_2{\cdot}CMe(COOEt)_2$, can be obtained from ethyl sodiomethylmalonate and ethyl chloracetate, or from ethyl sodioethenyltricarboxylate and methyl iodide; it boils at 273·5° (corr.), and on analysis yields methylsuccinic acid (m. p. 112°).

Ethyl butenyltricarboxylate, COOEt·CHEt·CH(COOEt)$_2$, obtained from ethyl sodiomalonate and ethyl α-bromobutyrate, boils at 278° (corr.), and gives ethylsuccinic acid (m. p. 98°) on hydrolysis.

Ethyl isobutenyltricarboxylate, COOEt·CMe$_2$·CH(COOEt)$_2$, prepared from ethyl sodiomalonate and ethyl α-bromisobutyrate, boils at 277·3° (corr.); on hydrolysis, it yields asymmetrical dimethylsuccinic acid (m. p. 140°) and small quantities of an acid of lower melting point, but no methylglutaric acid.

Ethyl ethylethenyltricarboxylate, COOEt·CH$_2$·CEt(COOEt)$_2$, obtained from ethyl sodioethylmalonate and ethyl chloracetate, or from ethyl sodioethenyltricarboxylate and ethyl iodide, boils at 281·5° (corr.), and gives ethylsuccinic acid (m. p. 98°) on hydrolysis. F. S. K.

The Two Symmetrical Dimethylsuccinic Acids. By C. A. Bischoff and E. Voit (*Ber.*, **23**, 639—644; compare Abstr., 1889, 490). —Ethyl methylpropenyltricarboxylate, COOEt·CHMe·CMe(COOEt)$_2$, prepared from ethyl sodiomethylmalonate and ethyl α-bromopropionate, or from methyl iodide and ethyl sodiopropenyltricarboxylate, boils at 279° (corr.), and on hydrolysis gives symmetrical para- and anti-dimethylsuccinic acids melting at 194° and 120° respectively (*loc. cit.*). Anti-dimethylsuccinimide, $C_6H_9O_2N$, crystallises in concentrically grouped needles or hexagonal plates, and is readily soluble in water, alcohol, benzene, chloroform, and acetone, but only sparingly in ether, and very sparingly in light petroleum.

F. S. K.

Relation of the Two Symmetrical Dimethylsuccinic Acids to Pyrocinchonic Acid. By C. A. Bischoff and E. Voit (*Ber.*, **23**, 644—646).—The fact that pyrocinchonic acid on reduction yields the two symmetrical dimethylsuccinic acids is in accordance with Wislicenus' hypothesis.

When para- or anti-dimethylsuccinic acid is treated with bromine, it is converted into pyrocinchonic acid; the anhydrides of both para- and anti-dimethylsuccinic acid yield pyrocinchonic acid on heating at 90—100° with bromine in chloroform solution. F. S. K.

Symmetrical Ethylmethylsuccinic, Trimethylsuccinic, Symmetrical and Asymmetrical Diethylsuccinic, and Ethyldimethylsuccinic Acids. By C. A. Bischoff and N. Mintz (*Ber.*, **23**, 647—652).—Ethyl methylbutenyltricarboxylate,

COOEt·CHEt·CMe(COOEt)$_2$,

prepared from ethyl sodiomethylmalonate and ethyl α-bromobutyrate, or from ethyl sodiobutenyltricarboxylate and methyl iodide, boils at 281·5° (corr.), and on hydrolysis yields symmetrical para- and meso-ethylmethylsuccinic acids.

Ethyl ethylpropenyltricarboxylate, COOEt·CHMe·CEt(COOEt)$_2$, prepared from ethyl sodioethylmalonate and ethyl α-bromopropionate, or from ethyl sodiopropenyltricarboxylate and ethyl iodide, boils at 282·8° (corr.), and on hydrolysis yields the two symmetrical ethylmethylsuccinic acids.

Ethyl methylisobutenyltricarboxylate, COOEt·CMe$_2$·CMe(COOEt)$_2$, is best prepared from ethyl sodiomethylmalonate and ethyl α-bromisobutyrate; it boils at 284·3° (corr.), and on hydrolysis gives trimethylsuccinic acid (m. p. 105°) and traces of higher melting acids.

Ethyl ethylbutenyltricarboxylate, COOEt·CHEt·CEt(COOEt)$_2$, obtained from ethyl sodioethylmalonate and ethyl α-bromobutyrate, or from ethyl sodiobutenyltricarboxylate and ethyl iodide, boils at 285·5° (corr.), and on hydrolysis gives para- and anti-diethylsuccinic acid and an acid melting at 137·5° (compare *Ber.*, **21**, 2109).

Ethyl isohexenyltricarboxylate, COOEt·CEt$_2$·CH(COOEt)$_2$, prepared from ethyl sodiomalonate and ethyl α-bromodiethylacetate, boils at 289·3° (corr.), and on hydrolysis gives asymmetrical diethylsuccinic acid (m. p. about 86°).

Ethyl ethylisobutenyltricarboxylate, COOEt·CMe$_2$·CEt(COOEt)$_2$, is best prepared by treating ethyl sodioethylmalonate with ethyl α-bromisobutyrate. It boils at 294·3° (corr.), and on hydrolysis gives two ethyldimethylsuccinic acids, melting at 63° and 105° respectively.

F. S. K.

Anhydride Formation and Intramolecular Change of Substituted Succinic Acids. By C. A. Bischoff and N. Mintz (*Ber.*, **23**, 656—659).—All the substitnted succinic acids examined by the authors lose water at a high temperature (200—300°), and are converted into anhydrides; in some cases the anhydride formed is not that of the original acid, but that of the geometrical or dynamical isomeride.

The monosubstitnted and the asymmetrical disubstituted succiuic acids undergo no change when heated in sealed tubes at 200°, but the symmetrical disubstituted acids are partially converted into the geometrical or dynamical isomerides, so that a mixture of the two is formed.

On heating with concentrated hydrochloric acid at 200° in sealed tubes, antidimethyl-, antidiethyl-, and mesobenzyl-ethylsuccinic acids are converted into the corresponding para-acids; ethyldimethylsuccinic acid (m. p. 63°) under these conditions is converted into the dynamical isomeride.

F. S. K.

Rotatory Power of Compounds of Malic Acid with Normal Lithium and Magnesium Molybdates. By D. Gernez (*Compt. rend.*, **110**, 529—532).—The solutions examined contained 1·1166 gram of lævogyrate malic acid, various proportions of the molybdate, and sufficient water to make the total volume up to **12** c.c. The rotatory power of the malic acid alone, in a tube 105·7 mm. long, was $-0° 11'$.

With lithium molybdate, the increase in rotatory power is at first practically proportional to the quantity of salt added, and attains a first maximum at $-10° 8'$, which corresponds with equal equivalents of the malic acid and the molybdate. On the addition of more molybdate, the rotatory power decreases, changes in sign, and increases, reaching a second maximum at $+15° 36'$, when the liquid contains 4 equivalents of malic acid to 9 of the molybdate. Further

quantities of salt cause diminution in rotatory power and a change of sign, a third maximum being reached at $-2° 22'$, when the solution contains 4 equivalents of molybdate to 1 of malic acid. The continued addition of molybdate causes another change of sign, and the rotatory power increases to $+8° 10'$, and even then has not reached its limit.

With magnesium molybdate, the phenomena are of the same order. A first maximum is reached at $-9° 40'$ with equal equivalents of acid and salt. This is followed by a diminution in rotatory power, followed by a change of sign and a second maximum at $+18° 14'$, with 4 equivalents of acid to 9 of molybdate. Further addition of molybdate causes a second reduction, with a minimum at $+1° 6'$ when the liquid contains 4 equivalents of molybdate to 1 of malic acid. Beyond this point an increase in the proportion of the molybdate increases the rotatory power, which has not reached its limit even at $+8° 44'$ (compare Abstr., 1887, 540; 1888, 97 and 938; and 1889, 1147). C. H. B.

Physical Constants of Alkyl-derivatives of Ethyl Ethenyltricarboxylate. By C. H. Bischoff and P. Walden (*Ber.*, 23, 660—664).—In the following table (next page) are given some physical constants of various derivatives of ethyl ethenyltricarboxylate.

The atoms and groups combined to the atomic complex

$$COOEt{\cdot}C\beta_2{\cdot}C\alpha(COOEt)_2$$

are given in column 2. The molecular weight is given in column 3, the boiling point (corr.) in column 4, and the sp. gr. at 20°, reduced to a vacuum and water at 4°, in column 5. Column 6 gives the refractive index for the D-line (at 19—20°), column 7 the molecular refractive energy calculated from the experimental data by means of the formula $\frac{M(n^2-1)}{d(n^2+2)}$, and column 8 the molecular refractive energy calculated from Conrady's values ($C = 2{\cdot}5$, $H = 1{\cdot}05$, $O' = 1{\cdot}68$, $O'' = 2{\cdot}29$). Column 9 gives the molecular refractive energy calculated from the experimental data by means of the formula $M\frac{n-1}{d}$, and column 10 the molecular refractive energy calculated from the values $C = 5$, $H = 1{\cdot}3$, $O' = 3{\cdot}4$, $O'' = 2{\cdot}8$. Column 11 gives the angle of dispersion (observed with an Abbe's refractometer), and column 12 the molecular volume calculated from the experimental data.

The following table shows that, with the exception of ethyl ethenyltricarboxylate, the boiling point increases with the molecular weight; in the case of isomerides, the boiling point is influenced by the position of the alkyl radicles, and is altered by the replacement of an ethyl- by two methyl-groups.

The author's observations confirm Brühl's conclusions respecting the specific gravity and the specific and molecular refractive energy of isomeric compounds. F. S. K.

1.	2.			3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
	α.	β.	β.	M.W.	B.P.	$d\frac{20°}{4\text{ vac.}}$	n_D.	$\frac{M}{d}\cdot\frac{n^2-1}{n^2+2}$.	$\frac{M}{d}\cdot\frac{n^2-1}{n^2+2}$.	$\frac{M}{d}\cdot(n-1)$.	$\frac{M}{d}\cdot(n-1)$.	Dispersion. $z°$.	μ.
Ethenyl	H	H	H	246	278·3	1·0952	1·4315	58·20	58·31	96·9	97·0	36·7	224·6
Propenyl	H	Me	H	260	270·3	1·0698	1·4288	62·63	62·91	104·2	104·6	36·7	243·0
Methylethenyl ...	Me	H	H	260	273·5	1·0767	1·4311	62·52	62·91	104·1	104·6	36·4	241·5
Isobutenyl	H	Me	Me	274	277·3	1·0607	1·4325	67·07	67·51	111·7	112·2	36·6	258·3
Butenyl	H	Et	H	274	278·0	1·0583	1·4321	67·16	67·51	111·9	112·2	36·5	258·9
Methylpropenyl..	Me	Me	H	274	278·8	1·0655	1·4334	66·89	67·51	111·5	112·2	36·4	257·2
Ethylethenyl	Et	H	H	274	281·3	1·0656	1·4338	66·93	67·51	111·5	112·2	36·7	257·1
Methylbutenyl ..	Me	Et	H	288	281·8	1·0523	1·4340	71·27	72·11	118·8	119·8	36·7	273·7
Ethylpropenyl ..	Et	Me	H	288	282·8	1·0607	1·4373	71·17	72·11	118·7	119·8	36·4	271·5
Methylisobutenyl	Me	Me	Me	288	284·3	1·0524	1·4333	71·16	72·11	118·6	119·8	36·6	273·7
Ethylbutenyl	Et	Et	H	302	285·1	1·0472	1·4355	75·34	76·71	126·6	127·4	36·7	288·4
Isohexenyl	H	Et	Et	302	289·3	1·0447	1·4373	75·78	76·71	126·4	127·4	36·4	289·1
Ethylisobutenyl..	Et	Me	Me	302	294·3	1·0435	1·4372	75·83	76·71	126·5	127·4	36·7	289·3
Benzylethenyl ...	Bz	H	H	336	336·3	1·1079	1·4844	86·83	87·24	146·9	147·0	35·7	303·3
Benzylpropenyl..	Bz	Me	H	350	337·8	1·1003	1·4850	91·17	91·84	154·3	154·6	35·6	317·5
Benzylbutenyl ..	Bz	Et	H	364	336·1	1·0899	1·4867	96·00	96·44	162·5	162·2	35·3	332·3
Benzylisobutenyl.	Bz	Me	Me	364	336·6	1·0950	1·4884	95·84	96·44	162·4	162·2	35·5	334·0

Attempts to prepare Alkyl Substituted Tricarballylic Acids. By C. A. BISCHOFF and A. v. KUHLBERG (*Ber.*, **23**, 664—669).—A small quantity of a thick, yellow oil boiling at 315—334° is obtained when the crude product of the action of ethyl sodioisobutenyltricarboxylate and ethyl α-bromisobutyrate is fractionated. On hydrolysis, this oil yields *tetramethyltricarballylic acid*,

$$COOH\cdot CMe_2\cdot CH(COOH)\cdot CMe_2\cdot COOH,$$

which separates from a mixture of benzene and acetone in colourless crystals melting at 156°.

When ethyl sodiobutenyltricarboxylate is treated with ethyl α-bromopropionate, an oil of the composition $C_{16}H_{30}O_8$ is formed in small quantities. F. S. K.

Preparation of Betaïnes. By E. DUVILLIER (*Compt. rend.*, **110**, 640—642).—Betaïnes are readily obtained with but slight admixture with secondary products by the action of alkyl iodides on zinc salts of the amido-acids in presence of zinc oxide.

4 parts of methyl iodide, 1 part of zinc amidoisovalerate, and 1 part of zinc oxide are heated in sealed tubes at 100—110°. After 16 to 18 hours, the amidovalerate and zinc oxide have disappeared; the product is boiled with water, treated with barium sulphide to remove the zinc, sulphuric acid to remove the barium, and silver hydroxide to eliminate iodine. The liquid is then treated with hydrochloric acid and platinum chloride. It yields a slightly orange-yellow platinochloride which is insoluble in alcohol, but moderately soluble in warm water, from which it separates in oblique, transparent prisms with 2 mols. H_2O or 4 mols. H_2O. The aurochloride crystallises in deep-yellow, anhydrous leaflets, moderately soluble in warm water, soluble in alcohol, insoluble in ether free from alcohol. No tetramethylammonium hydroxide is formed in the preparation of the betaïne in this way. C. H. B.

α- and β-Homobetaïne. By J. WEISS (*Arch. Pharm.* [3], **28**, 186—191).—α-Homobetaïne is best obtained by the action of methyl iodide on α-alanine in alkaline solution. The platinochloride crystallises in the monoclinic system $\breve{a} : \bar{b} : \acute{c} = 0{\cdot}8100 : 1 : 0{\cdot}6214$; $\beta = 74° \ 18' \ 34''$. Mean index of refraction for sodium light, 1·6555. Brühl previously obtained α-homobetaïne by the action of trimethylamine on ethyl α-chloropropionate.

β-Homobetaïne, $OH\cdot NMe_3\cdot CH_2\cdot CH_2\cdot COOH$, is best obtained by heating β-iodopropionic acid with excess of a 33 per cent. solution of trimethylamine for six hours at 100°. The solution remains clear when cold, but after evaporation, a white, crystalline mass is obtained. This product is dissolved in water and digested with excess of silver chloride, and the chloride thus produced converted into the platinochloride. The crystalline form of this salt is monoclinic, $\breve{a} : \bar{b} : \acute{c} = 1{\cdot}3484 : 1 : 1{\cdot}0659$; $\beta = 88° \ 45' \ 3''$. The aurochloride was also prepared and analysed. J. T.

Preparation of Ethylsulphonic Acid. By F. MAYER (*Ber.*, **23**, 908—912).—Ethylsulphonic acid is best prepared by heating sodium ethyl sulphate (1 part) with sodium sulphite (2 parts) and water (1 part) under pressure at 110—120° for three to four hours. The liquid is separated from the sodium sulphate by filtration, evaporated to dryness, the residue extracted with a large quantity of hot alcohol, and the filtered alcoholic solution allowed to cool, whereon sodium ethylsulphonate separates in small plates or needles. The sodium salt crystallises with 1 mol. H_2O; the double salt, $4C_2H_5 \cdot SO_3Na,NaI + H_2O$, does not lose its water at 160°; the barium salt crystallises with 2 mols. H_2O; the chloride boils at 171—173°. F. S. K.

Conversion of Allylbenzene- into Propenylbenzene-derivatives, their Dispersion and Refraction. By J. F. EYKMAN (*Ber.*, **23**, 855—864; compare this vol., p. 135).—Cubebin has the molecular formula $C_{20}H_{20}O_6$, as is shown by molecular weight determinations by Raoult's method; an optical examination of this compound showed that its dispersion is normal.

That apiole and isapiole have the same molecular formula was proved by determining the vapour-density of apiole under reduced pressure by means of the apparatus previously described (this vol., p. 101), and by determining the molecular weight of isapiole by Raoult's method; measurements of the dispersion of these two compounds seem to show that apiole is an allyl-, isapiole a propenyl-derivative.

All compounds such as safrole, methyleugenol, ethyleugenol, ethylchavibetole, &c., which contain the normal allyl-group, on prolonged boiling with alcoholic potash, are converted into the corresponding propenyl-derivatives, identical in all respects with the propenyl-derivatives obtained in other ways; methylchavicole, for example, is converted into anethoïl, safrole into isosafrole, methyleugenol into methylisoeugenol, &c.

The author has measured the dispersion of a number of allyl- and propenyl-benzene-derivatives, including those named above; his results, which are given in tabular form, show that all those compounds which contain an allyl-group have a normal dispersion, whilst in the case of those which contain the propenyl-group, both the dispersion and the refraction are abnormally high. The dispersion is almost constant in each series, but about $1\frac{1}{2}$ times as great in the propenyl- as in the allyl-series. The dispersion of the alkyl-derivatives of the allylhydroxy-benzene-derivatives is less than that of the corresponding phenol, and decreases with the number of methyl-groups; no such difference is exhibited by the propenyl-benzene-compounds. The specific dispersion of the allyl-derivatives is almost constant, but that of the propenyl-compounds is the smaller the greater the specific gravity; for this reason, a comparison of the simple dispersions seems to be preferable to that of the specific dispersions. The entrance of oxygen into the molecule increases the specific gravity considerably, whilst the dispersion is only slightly influenced; a change in the position of the double binding, on the

other hand, increases the dispersion considerably, but has little effect on the specific gravity. F. S. K.

Formation of Thiocyanates from Amido-compounds. By L. GATTERMANN and W. HAUSSKNECHT (*Ber.*, **23**, 738—739).—Up to the present few compounds are known in which the thiocyanogen-group, S·CN, is directly attached to the benzene-ring. The authors have found that such compounds may be readily obtained by the action of diazo-salts on cuprous thiocyanate according to Sandmeyer's method. Unlike the latter, however, the authors recommend decomposing the diazo-salt in the cold, as follows:—

31 grams of aniline are dissolved in 100 grams of sulphuric acid and 200 grams of water, and diazotised in the usual manner. To this solution, a concentrated solution of potassium thiocyanate is added, and then gradually, a paste of cuprous thiocyanate, obtained by dissolving a mixture of 80 grams of cupric sulphate and 150 grams of ferrous sulphate in water, precipitating with 35 grams of potassium thiocyanate, and filtering. The reaction with the diazo-compound takes place in the cold, and is accelerated by stirring. After three hours, the phenyl thiocyanate is driven over with steam, and purified by rectification. The yield is very good, whereas by Billeter's method of acting on the lead salt of thiophenol with cyanagen chloride or iodide only small quantities are obtained. The compound is indeed so readily prepared that thiophenol may be most easily obtained from it by treatment with potassium hydrosulphide.

Other derivatives, such as ortho- and paratolyl- and α-naphthyl thiocyanates have been prepared by this method. Isocyanates may also be prepared in a similar manner, but the yield is not so satisfactory. H. G. C.

Preparation of Aromatic Thiocyanates. By G. THURNAUER (*Ber.*, **23**, 769—772).—Paratolyl thiocyanate may be obtained in a manner similar to phenyl thiocyanate (Billeter, this Journ., 1875, 464) by passing cyanogen chloride through lead thiocresoxide suspended in alcohol. Some tolyl disulphide is also formed, but crystallises out when the oil obtained by filtering and evaporating the alcoholic solution is allowed to remain in the cold. Paratolyl thiocyanate is an oil of sweetish, unpleasant odour, which boils at 245—250° (765·5 mm.), and solidifies in a freezing mixture forming a crystalline mass. It may also be obtained by the action of cyanogen chloride on sodium thiocresoxide, if all water be carefully excluded. If cyanogen bromide and iodide be substituted for the chloride, the chief product, both with the lead and the sodium salt, is tolyl disulphide, only traces of the thiocyanate being formed.

The author has also obtained thiocyanates by Sandmeyer's method (compare previous abstract). The diazotised solution is prepared according to Sandmeyer's method, and allowed to flow into a cold solution containing 18 grams of cuprous thiocyanate, 85—90 grams of potassium thiocyanate, and 50 grams of water. After remaining for some hours the mixture is extracted with ether, and the ethereal

solution washed with dilute acid and alkali, filtered. and the ether evaporated, the residual oil being purified by fractional distillation under reduced pressure.

The *paratolyl thiocyanate* prepared by this method from paratoluidine was identical with the oil above described. *Orthotolyl thiocyanate*, C_7H_7SCN, is a yellowish-red oil, boiling at 243—246°, and having an unpleasant smell. Both these compounds cause violent itching of the hands, which continues for some time after ceasing to work with them.

Contrary to the statement of Gattermann and Hausknecht (previous abstract) the author finds that a paste of cuprous thiocyanate has no action on diazotoluene either in the cold or at a higher temperature. H. G. C.

Diphenyl Carbonate. By H. ECKENROTH and J. RÜCKEL (*Ber.*, **23**, 693—701).—The reactions of phenyl carbonate, which have been previously examined by Kempff (this Journ., 1871, 341), Hentschel (*Ber.*, **17**, 1287), and Eckenroth (Abstr., 1885, 786), have been further investigated by the authors, with the following results. In preparing diphenylcarbamide from phenyl carbonate, it is unnecessary to heat the latter with aniline under pressure, as the reaction takes place equally well when the two substances are heated together in a reflux apparatus for 2—3 hours. Ortho- and para-diphenylcarbamide and dinaphthylcarbamide may be prepared in a similar manner.

Chlorine and iodine do not combine directly with phenyl carbonate, but if the latter be heated with an excess of bromine at 100°, until no more gas is evolved, a white mass remains on evaporating off the excess of bromine, which crystallises from alcohol in long, silky needles melting at 169°, and having the composition $(C_6H_4Br)_2CO_3$. It is readily soluble in benzene, chloroform, acetone, and ether, sparingly in cold light petroleum and alcohol, and insoluble in water.

It has been previously shown by Eckenroth (Abstr., 1885, 786) that diphenyl carbonate and diphenylcarbamide act on one another with formation of phenyl cyanate and phenol, and that these then again combine together to form phenyl phenylcarbamate (compare Snape, Trans., 1885, 770). The same reaction takes place if para- or orthoditolylcarbamide is substituted for diphenylcarbamide, and in these cases also the reaction is very incomplete. 8 grams of paraditolylcarbamide (obtained by boiling diphenyl carbonate with paratoluidine, washing the product with alcohol, and crystallising from the same liquid) was mixed with 7 grams of diphenyl carbonate and distilled, the distillate being allowed to remain for 14 days. The crystals formed were separated from the adhering oil, recrystallised several times from light petroleum, and thus obtained as slender, white needles melting at 115°, and agreeing in composition with the expected phenyl paratolylcarbamate $CH_3{\cdot}C_6H_4{\cdot}NH{\cdot}COOPh$.

For the preparation of phenyl orthotolylcarbamate, 8 grams of orthoditolylcarbamide (obtained in a similar manner to the paracompound) were boiled with 7 grams of phenyl carbonate in a reflux apparatus for several hours, and two-thirds of the mixture then slowly

distilled over, the distillate being allowed to remain for 14 days, and treated as in the foregoing case. The phenyl orthotolylcarbamate thus obtained forms crystals which melt at 92°.

Attempts to prepare the corresponding thiocarbamates in a similar manner failed on account of the difficulty of separating the compounds formed. H. G. C.

ɛ-Dinitrophenol. By V. WENDER (*Gazzetta*, **19**, 218—224).—The constitution of this compound, which was first prepared by Bantlin (Abstr., 1879, 237), has not yet been elucidated, but since Henriques found (Abstr., 1883, 327) that the corresponding anisoïl, when treated with ammonia, yields a nitroanisidine from which metanitroanisoïl may be prepared by eliminating amidogen, it must have the constitution [$(NO_2)_2$ = 2 : 3 or 3 : 5]. The 2 : 3 formula appears the more probable, as it explains the transformation into nitranisidine, where the nitroxyls are already in ortho-position.

The author has therefore endeavoured to prepare the 3·5-dinitrophenol by diazotising dinitranisidine [$(NO_2)_2 : NH_2$ = 3 : 5 : 4], prepared by the nitration of paranisidine, or by the action of ammonia on the dimethyl ether obtained from the dinitroquinol [$(OH)_2 : (NO_2)_2$ = 1 : 4 : 3 : 5] melting at 135°. The following compounds were prepared in the course of the experiments.

Dinitroparaphenacetide, $C_6H(NO_2)_2(OEt)\cdot NHAc$, prepared by dissolving paraphenacetide in glacial acetic acid (5 parts), cooling to 5°, and adding nitric acid (1 part, sp. gr. = 1·54). On dilution with water, the dinitrophenacetide is thrown down as a crystalline powder, which crystallises from alcohol in lustrous, silky needles, and from acetic acid in prisms. It melts at 206°, and is freely soluble in acetic acid, especially on warming, and in ether, very moderately in boiling alcohol, and very sparingly in cold alcohol. Hydrolysis does not take place on boiling it with hydrochloric acid, potash partially saponifies it in the cold, but on heating ammonia is evolved. It may also be prepared from the mononitro-derivative (melting at 104°). One of the nitroxyl-groups in this substance must occupy a meta-position relatively to the ethoxyl as in the mononitro-derivative.

Dinitrophenetidine, $C_6H_2(NO_2)_2(OEt)\cdot NH_2$. The preceding compound is hydrolysed by heating for 10 minntes with concentrated sulphuric acid (8 parts), the temperature not exceeding 100°. On diluting with water, the base is precipitated in red flakes which crystallise out from alcohol in thin, brownish-red prisms melting at 145°. It has feeble basic properties; the hydrochloride and sulphate may be obtained in an ethereal or acetic acid solution, but they are decomposed by cold water.

Dinitracetaniside, $C_6H_2(NO_2)_2(OMe)\cdot NHAc$, is prepared like the ethyl-compound, starting with the nitracetaniside, melting at 116°. It resembles the ethyl-derivative in many respects, forming long, slender, flat, brilliant, pale-yellowish needles which melt at 220°. It is soluble in hot acetic acid, only moderately so in boiling alcohol, very sparingly in cold alcohol, whilst it is almost insoluble in boiling water.

Dinitranisidine, $C_6H_2(NO_2)_2(OMe)\cdot NH_2$, is obtained by heating the preceding compound with concentrated sulphuric acid for 15 minutes, and diluting with water. The orange-coloured precipitate which is formed crystallises from boiling alcohol in bright-crimson needles with a bluish sheen, and melts at 182° to a red liquid. It is freely soluble in alcohol, acetic acid, and ether, and moderately in boiling water. When heated with aqueous potash, it dissolves with evolution of ammonia.

Dinitromethylquinol is formed as a secondary product of the action of ethyl nitrite on dinitranisidine. A solution of this substance (30 grams) in absolute alcohol (600 grams) is saturated with nitrous anhydride, and heated for 24 hours in a reflux apparatus. The ethyl nitrite is then distilled off, and the residue exhausted with a boiling solution of potassium carbonate, the cold solution being extracted with ether, acidified, and again treated with ether; the second extract contains the quinol, which crystallises from boiling alcohol in bright-yellow, lustrous tables, melts at 110°, and dissolves freely in hot alcohol, less so in cold; it is also soluble in acetic acid and in ether. The *barium derivative* forms lustrous, lemon-yellow needles, freely soluble in boiling water, sparingly in cold. A small proportion of this quinol is also formed when dinitranisidine is diazotised, and the resulting salt decomposed with dilute sulphuric acid.

ε-Dinitroanisoïl is the principal product of the action of ethyl nitrite on dinitranisidine (m. p. 182°); the portion insoluble in potassium carbonate crystallises from alcohol in faintly-yellowish plates which melt at 119°, and with care can be distilled without decomposition; if rapidly heated, however, it explodes. It is soluble in boiling water and in hot alcohol, less so in cold alcohol and in boiling light petroleum. It is not volatile in steam. When heated with alcoholic ammonia for 5 hours at 180°, it is converted into Bantlin's nitranisidine, melting at 75°; this yields metanitranisoïl when heated with ethyl nitrite.

ε-Dinitrophenol is obtained by heating the preceding compound with hydrochloric acid at 150° for 24 hours. The product is evaporated to dryness, extracted with a boiling solution of potash, the solution treated with ether, acidified, and again extracted with ether. The latter extract contains the dinitrophenol, which crystallises from alcohol in bright-yellow tables; it melts at 144—145°, and has an odour resembling that of metanitrophenol. It is freely soluble in ether and hot alcohol, and moderately in boiling water. The *barium derivative* is soluble in hot water, and separates out in slender, golden needles, or in groups of brownish-yellow needles, according as the solution is rapidly cooled or slowly evaporated. On heating to 150°, it becomes brownish-red, changing back to a dirty-yellow on cooling. The *potassium derivative* crystallises from water in slender, orange needles, or in thin, lustrous laminæ, containing 2 mols. H_2O, and is freely soluble in hot water and moderately in cold; when anhydrous it is of a deep-scarlet colour. By treatment with nitric acid, this dinitrophenol yields styphnic acid (m. p. 175°). It therefore appears that the phenol and anisoïl obtained are identical with Bantlin's ε-compounds.

S. B. A. A.

Constitution of Bromonitrothymol, Dinitrothymol, Dinitramidocymene, Dinitrocymene, and the Isomeric Chloro- and Bromo-thymoquinones. By G. Mazzara (*Gazzetta*, 19, 160—169). —When the ethyl ether of dinitrothymol is heated with alcoholic ammonia for 10 hours in a closed tube at 180—190°, and the product is freed from ammonia and crystallised from dilute alcohol, a dinitramidocymene, $C_6HPrMe(NO_2)_2\cdot NH_2$, is obtained in large, dark-yellow prismatic tables which soften at 108°, melt at 113—115°, dissolve sparingly in light petroleum and in hot water, separating out, on cooling, in small laminæ which volatilise with some difficulty in a current of steam.

According to Bantlin (Abstr., 1879, 237), only the 3·5-dinitranisoïl yields a dinitraniline when heated with alcoholic ammonia (compare Abstr., 1883, 327); the structure of the ethyl ether of dinitrothymol must therefore be—

$$[Me : NO_2 : OEt : Pr : NO_2 = 1 : 2 : 3 : 4 : 6],$$

and that of dinitramidocymene—

$$[Me : NO_2 : NH_2 : Pr : NO_2 = 1 : 2 : 3 : 4 : 6].$$

The ethyl ether of nitrobromothymol, heated with alcoholic ammonia in a sealed tube at 180—190° for 14 hours, undergoes no change; it thus behaves as a meta-derivative, and in order that the bromine should be in a meta-position with respect to the nitroxyl, the latter must be in a para-position with respect to the hydroxyl. The structure of bromonitrothymol is therefore $[Me : Br : OH : Pr : NO_2 = 1 : 2 : 3 : 4 : 6]$. This is confirmed by the fact that on nitration it yields dinitrothymol, the ethyl ether of which has been shown above to have its nitroxyls in the meta-position (relatively to each other). Further support is derived from the following considerations:—(1) the same nitrobromo-derivative is obtained by brominating nitrothymol and by nitrating parabromothymol, a result only explicable on the assumption that in the latter reaction the nitroxyl displaces the bromine; (2) that the corresponding amidobromothymol (Abstr., 1886, 1016) yields, with nitrous acid, a bromothymoquinone, which has its two oxygen-atoms in the para-position.

When dinitroamidocymene is treated with alcohol containing ethyl nitrite, the product distilled in a current of steam, pressed between filter-paper, and crystallised from dilute alcohol, a compound is obtained in rhombohedral plates which melt at 54°, and to all appearance is identical with Kraut's dinitrocymene, $[Me : Pr : (NO_2)_2 = 1 : 4 : 2 : 6]$.

Bromothymoquinone.—A bromothymoquinone melting at 48° was prepared from amidobromothymol hydrochloride, and, on reduction with sulphurous anhydride, yielded a bromothymoquinol melting at 52—53° (Abstr., 1886, 1016). The same substance is obtained by the action of potassium nitrite on amidobromothymol prepared from parabromothymol. This quinone and quinol must, from their formation, respectively have the constitutions

$$[Me : Br : O : Pr : O = 1 : 2 : 3 : 4 : 6]$$
and $$[Me : Br : OH : Pr : OH = 1 : 2 : 3 : 4 : 6].$$

Schniter (Abstr., 1887, 720) describes a bromothymoquinol (m. p. 53°) which yields a quinone melting at 45°; to the former he ascribes the constitution [Br = 5], whereas he considers chlorothymoquinol to have the structure [Cl = 2]. The formation of the same chlorobromothymoquinol, whichever of the halogens is first introduced, is thus explained by assuming that the atoms of chlorine and bromine always displace different hydrogen-atoms. Schniter principally relies on the formation of a liquid chlorothymoquinol, which yields a chlorobromothymoquinone and quinol melting at a somewhat lower temperature than the isomeric derivatives from the solid chlorothymoquinol.

The author attaches no importance to the slight difference in melting point between Schniter's bromothymoquinone and his own, and considers that the agreement of the other physical properties of these compounds, and of the melting points of the corresponding quinols, is sufficient evidence of their identity. It would, therefore, appear that Schniter's distinction between $\alpha\beta$- and $\beta\alpha$-compounds is very doubtful. The author concludes that when a halogen acid acts on thymoquinone, the halogen takes the place of the hydrogen-atom next to the methyl [2]. Chlorine, however, displaces bromine from this position, leaving it to displace the atom of hydrogen next to the propyl [5], an action analogous to that of nitroxyl and bromine on thymol (compare this vol., p. 367). S. B. A. A.

Action of Chlorine on Catechol and Orthamidophenol. By T. ZINCKE and F. KÜSTER (*Ber.*, **23**, 812—831; compare Abstr., 1888, 1277, and 1889, 599).—The hexachlorohydroxypentenecarboxylic acid melting at 110°, described in a former paper, when heated at 120—140°, is found to be converted into an isomeric acid melting at 186°, which is very like the original acid in its chemical properties. When oxidised, it yields a ketone (hexachloroketopentene) melting at 92°, isomeric with that (m. p. 31°) obtained from the original acid; and this ketone, like its isomeride, is converted by treatment with alkalis into an acid, but a different one, of the formula $C_4Cl_5{\cdot}COOH$. The constitution of these two isomeric series is discussed at considerable length. The constitution of the members of the first series has been already determined, and the authors think that the members of the second series are not merely geometrical isomerides of the others, or derived from different hydrocarbons of the formula C_5H_6; they regard it as more probable that the isomerism is caused by a difference in the relative position of the chlorine-atoms in the five-atom carbon ring. They consequently assign the following formulæ to the compounds mentioned above (the Greek letters in brackets refer to the position of the double bond):—

	Hydroxy-acid.	Ketone.
First ($\beta:\gamma$) series	$\begin{matrix} CCl:CCl \\ \vert \\ CCl_2{\cdot}CCl_2 \end{matrix}\!>\!C(OH){\cdot}COOH$	$\begin{matrix} CCl:CCl \\ \vert \\ CCl_2{\cdot}CCl_2 \end{matrix}\!>\!CO.$
	Melting at 110°.	Melting at 31°.
Second ($\gamma:\gamma$) series	$\begin{matrix} CCl{\cdot}CCl_2 \\ \Vert \\ CCl{\cdot}CCl_2 \end{matrix}\!>\!C(OH){\cdot}COOH$	$\begin{matrix} CCl{\cdot}CCl_2 \\ \Vert \\ CCl{\cdot}CCl_2 \end{matrix}\!>\!CO.$
	Melting at 186°.	Melting at 92°.

The constitution of the $\beta:\gamma$-series was determined by the formation of propylideneacetic acid when the acid $C_4Cl_5{\cdot}COOH$, derived from the $\beta:\gamma$-ketone, was reduced with nascent hydrogen. This acid was, therefore, thought to be a pentachlorobutenecarboxylic acid of the formula $CCl_2{:}CCl{\cdot}CCl{:}CCl{\cdot}COOH$; but since Baeyer and Russe have shown that a change in the position of double bonds takes place in the case of hydromuconic acid, the above evidence is much weakened, and the authors propose to reinvestigate the subject.

The transformation of the $\beta:\gamma$-hydroxy-acid into the $\gamma:\gamma$-isomeride is complete; but the $\beta:\gamma$-ketone suffers a partial transformation only, and, indeed, the $\gamma:\gamma$-ketone is, to some extent converted by heat into the $\beta:\gamma$-isomeride. An acid, $C_4Cl_5{\cdot}COOH$, can be got only with difficulty from the $\gamma:\gamma$-ketone; it is necessary to work at 0°, and not to bring either the ketone or the acid directly into solution, as resinous matters are at once formed in an alkaline solution. The acid is altogether very unstable, and no satisfactory formula can be assigned to it. It is decomposed when gently heated, yielding carbonic anhydride and a substance C_4Cl_5H. When reduced, it yields an acid approximately of the composition $C_4H_7{\cdot}COOH$, but this acid acts as a strong reducing agent, and no conclusions can be drawn as to its constitution.

With phosphorus pentachloride, the $\beta:\gamma$-hydroxy-acid yielded a phosphate melting at 150°. The $\gamma:\gamma$-acid also yielded a phosphate, $COOH{\cdot}C_5Cl_6{\cdot}O{\cdot}PO_3H_2,2\frac{1}{2}H_2O$, melting at 170° when dried in air, at 152° when dried in a vacuum, and volatilising with decomposition at 215°. It also yields the $\gamma:\gamma$-ketone, the formation of which is attended by the evolution of hydrogen chloride and carbon monoxide.

A third substance, melting at 145°, was also obtained, but not in sufficient quantity to allow of its investigation.

The two ketones, when heated with phosphorus pentachloride, both gave the same $\gamma:\gamma$-octochloropentene, C_5Cl_8; but a high temperature was required, so that molecular transformation may have taken place.

With ammonia, the $\beta:\gamma$-ketone did not give an acid amide, but a substance was formed smelling like a carbamine, possibly of the formula $\begin{array}{l}CCl{:}CCl{-}CO\\ \vert\qquad\quad\ \ \vert\\ CCl_2{\cdot}CHCl{\cdot}NH\end{array}$. The $\gamma:\gamma$-ketone, however, gave the amide derived from the acid ($CCl_2{:}CCl{\cdot}CCl{:}CCl{\cdot}COOH$) formed by the action of soda on the $\beta:\gamma$-ketone. This is remarkable, for we have here the $\gamma:\gamma$-ketone transformed into a derivative of the otherwise less stable $\beta:\gamma$-ketone.

Hexachlorohydroxypentenecarboxylic acid ($\gamma:\gamma$) is obtained by heating the isomeric acid of melting point 110° at 120—140° for about an hour; the yield is about 80 per cent. of the theoretical. The molecular weight of the new acid was determined by Raoult's method, and it was thus shown that it is a true isomeride, and not a polymeride, of the original acid. It melts at 186°, and resembles the $\beta:\gamma$-acid in its chemical properties. Its barium salt crystallises with 2 mols. H_2O. The methyl salt melts at 119°. With acetic

chloride, it gives an *acetyl*-derivative melting, when dry, at 130°, the barium salt of which was prepared. When heated with bromine at 100°, bromopentachloroketopentene, C_5Cl_5BrO, is formed; the same substance is formed when the $\beta:\gamma$-hydroxy-acid is treated with bromine, and we have here another instance of the conversion of a $\beta:\gamma$- into a $\gamma:\gamma$-derivative. C. F. B.

Quinoneimides and Amidoquinones. By F. KEHRMANN (*Ber.*, 23, 897—907).—When chloroparadihydroxyquinone [$O_2 : (OH)_2 : Cl = 1 : 4 : 2 : 5 : 3$] is heated for a short time with aniline in alcoholic solution, it yields chlorodianilidoquinone, identical with the compound (m. p. 260—265°) obtained in like manner from metadichloroquinone by Niemeyer (Abstr., 1885, 1065). The action of free aniline on chloroparadihydroxyquinone is, therefore, the same as the action of aniline on paradihydroxyquinone (Nietzki and Schmidt, Abstr., 1889, 968); in the latter case, there is formed Hofmann's dianilidoquinone, which is, therefore, a paradianilido-compound.

When chloroparadihydroxyquinone is boiled with aniline in glacial acetic acid solution, it is converted into a compound, $C_{18}H_{13}ClN_2O_2$, isomeric with the compound melting at 260—265°. This substance crystallises in dark-green needles with a blue reflex, melts at about 240° with decomposition, and is moderately easily soluble in boiling glacial acetic acid and benzene, but only sparingly in alcohol and ether, and insoluble in water. It dissolves in concentrated sulphuric acid yielding a beautiful green solution; on diluting, the colour changes to blue, and on adding a large quantity of water, the anilide is precipitated unchanged. It is almost insoluble in alkalis, but it combines with them to form salts which are readily soluble in water with partial decomposition, but insoluble in dilute alkalis. When boiled with alcoholic potash, in which it is readily soluble, it is converted into a potassium salt, which remains, on evaporating the alcohol, in brownish-red needles; when this salt is boiled with dilute potash until the solution turns bright-red, aniline is liberated, and, on acidifying, a small quantity of a dark-green, crystalline substance is precipitated. This compound separates from boiling alcohol in small, bluish needles, has the composition $C_{12}H_8ClNO_3$, and is a chloro-derivative of a paranilidohydroxyquinone or of a paradihydroxyquinoneanilide; it is decomposed by boiling alkalis into aniline and chloroparadihydroxyquinone.

The behaviour and properties of the compound obtained by the action of aniline on chloroparadihydroxyquinone in glacial acetic acid solution show its complete analogy with the anilidohydroxyquinoneanilide and the anilidohydroxytoluquinoneanilide prepared by Zincke (Abstr., 1885, 787).

Anilidohydroxyquinoneanilide is converted into paradihydroxyquinone when heated with alkalis.

Zincke's dihydroxytoluquinone (Abstr., 1883, 1117) has probably the constitution [$O_2 : (OH)_2 : Me = 1 : 4 : 3 : 6 : 2$], as it is formed from its anilide in a manner similar to that in which the paradihydroxybenzoquinones are obtained, and the anilides of these

compounds, as well as the quinones themselves, behave in like manner.

When anilidohydroxyquinoneanilide or anilidohydroxyquinone is boiled with dilute potash for several hours, paradihydroxyquinone is formed, but only in small quantities, as it is itself gradually decomposed by potash. Hofmann's dianilidoquinone also yields paradihydroxyquinone on boiling with alcoholic sulphuric acid, and chlorodianilidoquinone gives chloroparadihydroxyquinone when treated in like manner.

Tetramethyldiamidoquinone (Mylins, Abstr., 1885, 803) is best prepared by treating chloroquinone with dimethylamine in alcoholic solution; when heated to boiling with dilute potash or hydrochloric acid, it is converted into paradihydroxyquinone, but when treated with cold dilute hydrochloric acid, it is converted into *dimethylamidohydroxyquinone* [$O_2 : NMe_2 : OH = 1 : 4 : 2 : 5$].

The above experiments show that all the compounds formed by the action of bases on benzoquinone are converted into one and the same paradihydroxyquinone by substituting the anilido- or amido- by hydroxy-groups, from which it may be concluded that the anilido- or amido-groups themselves are in the para-position to one another.

It may be stated, as a general rule, that by the action of amido-compounds on quinones of the type of benzoquinone, at the most two hydrogen-atoms in the nucleus can be substituted, and these two hydrogen-atoms are in the para-position one to the other; the compounds formed are, therefore, derivatives of paradiamidoquinone, and by their decomposition with acids or alkalis, paradihydroxy-derivatives of quinone and its homologues are produced.

F. S. K.

A Higher Homologue of Cholesterin. By F. MARINO-ZUCO (*Gazzetta*, 19, 209—212).—The ethereal extract of the flowers of *Chrysanthemum cinerariæfolium*, after repeated treament with aqueous and alcoholic potash, leaves a substance which forms yellow crystals melting at 70—100°. After repeatedly crystallising this from ether placed in a freezing mixture, melting under alcohol, and again crystallising from anhydrous ether, a paraffin ($C_{17}H_{36}$?) is obtained in very thin, colourless, nacreous scales; this melts at 64°, dissolves freely in ether, benzene, and chloroform, and moderately in hot alcohol, but is almost insoluble in cold alcohol.

The portion which remains dissolved in the cold ether is purified by fractional crystallisation, until the crystals which separate melt above 150°; the ethereal solution is then evaporated, when it leaves a residue, consisting of slender needles, of a substance resembling cholesterin, but containing small quantities of fats from which it cannot be freed by boiling with alcoholic potash. The *acetyl-derivative*, $C_{28}H_{47}\cdot OAc$, prepared by boiling the crude cholesterin with acetic anhydride, crystallises from alcohol and ether in colourless, nacreous scales which melt at 223°.

The *benzoyl-derivative*, $C_{28}H_{47}\cdot OBz$, obtained by heating the cholesterin with benzoic acid at 210—240°, crystallises from ether in small, colourless needles with a silky lustre which melt with decomposition at 246°.

The pure cholesterin, $C_{28}H_{48}O$, obtained by treating either of its derivatives with alcoholic potash, forms slender, colourless needles which melt at 183°, and gives all the reactions for cholesterin, including Hesse's reaction with sulphuric acid and chloroform. It dissolves freely in ether, benzene, and chloroform, and sparingly in hot alcohol, being deposited from the latter, on cooling, in a flocculent condition. S. B. A. A.

Properties of several Anilides. By A. PICTET (*Chem. Centr.*, 1890, i, 477—478; from *Arch. sci. phys. nat. Genève*, **22**, 508—522).—By boiling the alcoholic solution of formanilide with alcoholic potash and an alkyl iodide in a reflux apparatus, the alkylformanilides are obtained. The alkylacetanilides are obtained by warming the alkylformanilides with acetic anhydride. The alkylformanilides may also be saponified, and monalkylanilines obtained. The *alkylformanilides* are colourless, oily liquids at the ordinary temperature, without odour, but are strongly refractive, and have a burning taste. When distilled under the ordinary atmospheric pressure, they suffer decomposition more or less.

Of the *alkylacetanilides*, those of methyl, ethyl, propyl, and isopropyl are crystallisable substances.

The *monoalkylanilides* are liquids—

	Boiling point.	Under pressure in mm.	Sp. gr. at 16° (water at 4°).
Methylformanilide	253°	716	1·097
Ethylformanilide	258	728	1·063
Isopropylformanilide	261–263°	720	—
Propylformanilide	267°	731	1·044
Isobutylformanilide	274	731	—
Isoamylformanilide	285–286°	728	1·044

	Melting point.	Boiling point.	Under pressure.
Methylacetanilide	101°	253°	712
Ethylacetanilide	54	258	731
Isopropylacetanilide	38	262	728
Propylacetanilide	47–48°	266	716
Isobutylacetanilide	liquid	272–273°	712
Isoamylacetanilide	liquid	287°	730

	Boiling point.	Under pressure in mm.	Sp. gr. at 18° (water at 4°).
Methylaniline	191·0°	712	0·976
Ethylaniline	203·5	712	0·954
Isopropylaniline	207·0	731	—
Propylaniline	219·5	716	0·949
Isobutylaniline	229–230°	716	0 940
Isoamylaniline	252·5°	730	0·928

It is interesting to notice that the boiling points of the alkylacet-

anilides are exactly the same as those of the alkylformanilides, with which they correspond.

The following crystallographic determinations were also made:—Acetanilide, rhombic, 0·8481 : 2 : 2·067; methylacetanilide, rhombic, 2·530 : 1 : 2·149; ethylacetanilide, monoclinic, 1·32641 : 1 : x, β 101° 56′; phenylacetanilide, rhombic, 1·277 : 1 : 2·7917. J. W. L.

Syntheses by means of Phenyl Cyanate. By R. LEUCKART (*J. pr. Chem.* [2], 41, 301—329; compare Abstr., 1885, 773, 1224).—The preparation of anilides by the action of phenyl cyanate on hydrocarbons or alkyl phenyl ethers in the presence of aluminium chloride is best conducted as follows:—Phenyl cyanate (1 part) is mixed with the well-dried hydrocarbon or phenyl ether (10 parts), and aluminium chloride gradually added; when the mixture ceases to become hotter, it is heated on the water-bath until the smell of the cyanate disappears and hydrogen chloride begins to be evolved; at this point it is poured into water and the benzene solution separated and evaporated; the residue is extracted with boiling alcohol, the solution filtered and precipitated with water; the precipitate is warmed with an alkali, filtered, washed with water, dried, and distilled. The anilide which thus distils over is recrystallised from alcohol.

Paratoluanilide, from phenyl cyanate and toluene, crystallises in lustrous needles melting at 145° (compare Fischli, Abstr., 1879, 638, and Brückner, Abstr., 1881, 95).

Xylylanilide, from phenyl cyanate and metaxylene, crystallises in needles melting at 141° (compare Ador and Meier, Abstr., 1880, 252).

Isoxylylanilide, from phenyl cyanate and paraxylene, crystallises in colourless needles melting at 140°.

β-Isodurylanilide, $C_6H_2Me_3·CO·NHPh$, from phenyl cyanate and mesitylene, forms colourless needles melting at 165°, freely soluble in ether and hot alcohol.

Durylanilide, from phenyl cyanate and pseudocumene, crystallises in colourless needles melting at 178°.

Paradiphenylcarboxylanilide, $C_6H_4Ph·CO·NHPh$, from phenyl cyanate and diphenyl, forms colourless needles melting at 212°.

α-(?)-Naphthanilide, $C_{10}H_7·CO·NHPh$, from phenyl cyanate and naphthalene, crystallises in colourless needles melting at 161°, and is probably identical with Hofmann's so-called α-naphthanilide (m. p. 160°), but the acid obtained from it by fusion with potash melts at 140°, and is, therefore, not α-naphthoic acid (m. p. 160°).

Paratolylparatoluidide, $C_6H_4Me·CO·NH·C_6H_4Me$, obtained in like manner from paratolyl cyanate and toluene, crystallises in colourless needles melting at 158—159°.

The alkyl ethers of the phenols are conveniently prepared by dissolving the corresponding amine in alcohol, saturating with hydrogen chloride, and passing in the vapour of the alkyl nitrite; after all the nitrogen has been evolved the solution is evaporated, the residue washed with soda, dried, and distilled.

The action of phenyl cyanate on anisoïl, phenetoïl, and the naphthyl methyl ethers has been described already (Abstr., 1885, 1224).

Metamethylparamethoxybenzanilide, $MeO·C_6H_3Me·CO·NHPh$, prepared from phenyl cyanate and methyl orthocresyl ether, forms slender, lustrous, white needles melting at 147°; when fused with potash, it yields aniline and metamethylparamethoxybenzoic acid (m. p. 192°; Schall, Abstr., 1879, 792).

Metamethylorthomethoxybenzanilide, from methyl paracresyl ether and phenyl cyanate, crystallises in long, white, lustrous needles, melts at 96°, and is soluble in alcohol.

Methylpropylmethoxybenzanilide, $MeO·C_6H_2MePr·CONHPh$, from phenyl cyanate and methyl thymyl ether, crystallises in lustrous, long, white tables melting at 166°. When heated at 120—130° with strong hydrochloric acid, it yields *methylpropylmethoxybenzoic acid*, which crystallises in long, slender, lustrous needles melting at 140°; the constitution of this acid is uncertain, but it is probably identical with the acid obtained by Kobek by the methylation of parathymotic acid (Abstr., 1884, 56).

The action of phenyl cyanate on phenol has been studied by Hofmann (this Journal, 1871, 392).

Orthotolyl phenylcarbamate, $NHPh·COO·C_6H_4Me$, from phenyl cyanate and orthocresol, crystallises in long, slender, lustrous needles melting at 145° and soluble in hot alcohol.

Paratolyl phenylcarbamate forms lustrous, white leaflets, melts at 114°, and is soluble in hot alcohol.

Thymyl phenylcarbamate, $NHPh·COO·C_6H_3MePr$, from phenyl cyanate and thymol, forms lustrous, white needles melting at 104°.

The action of phenyl cyanate on α- and β-naphthol has been described before (Abstr., 1885, 1224); the melting point of β-naphthyl phenylcarbamate is 155—156°, not 230°.

Metanitrodiphenylcarbamide, $NHPh·CO·NH·C_6H_4·NO_2$, from phenyl cyanate and metanitraniline, melts at 198·5°. *Paranitrodiphenylcarbamide* melts at 212°. *Metamidodiphenylcarbamide* crystallises in small, grey needles melting at 187·5°; it has been obtained by Lellmann and Würthner (*Annalen*, **228**, 222; compare Abstr., 1885, 977).

Phenylmetanitroparatolylcarbamide, $NHPh·CO·NH·C_6H_3Me·NO_2$, from phenyl cyanate and metanitroparatoluidine, crystallises in small, lemon-yellow needles melting with decomposition at 194°.

Phenylorthamidotolylcarbamide, from phenyl cyanate and orthotolylenediamine, crystallises in colourless needles melting at 197—198°; its *hydrochloride, platinochloride*, and *sulphate* are described. When the hydrochloride is heated at 100°, it is decomposed into aniline and *tolylenecarbamide*, $C_6H_3Me<{NH \atop NH}>CO$, which forms slender needles, melts above 300°, and sublimes, undecomposed, in colourless leaflets. When the hydrochloride in aqueous solution is treated with potassium nitrite, *azimidotolylphenylcarbamide*, $C_6H_3Me·N_3·CONHPh$, is obtained; it forms colourless crystals melting at 159—160°; when it is treated with aqueous soda or potash, it is decomposed into phenyl cyanate and azimidotoluene (m. p. 85°), identical with Ladenburg's amidazotoluylene (m. p. 83°; this Journal, 1876, 933).

Diphenyltolylenedicarbamide, $C_6H_3Me(NPhH·CO·NH)_2$, is also ob-

tained when phenyl cyanate acts on orthotolylenediamine—especially if the temperature is high; it is left undissolved by alcohol, and crystallises from glacial acetic acid in small, sparingly soluble needles melting at 208—209°.

Orthohydroxydiphenylcarbamide, $NHPh\cdot CO\cdot NH\cdot C_6H_4\cdot OH$, is the product of the action of phenyl cyanate on orthamidophenol in ether; it forms crystals which melt at 165—166°, and are freely soluble; its *ethyl-derivative* melts at 169—170°. When orthohydroxydiphenylcarbamide is heated above its melting point, it is decomposed into aniline and oxycarbamidophenol (m. p. 141—142°; compare Kalckhoff, Abstr., 1883, 1110, who gives m. p. 137°).

Acetylorthamidophenyl phenylcarbamate, $NHPh\cdot CO\cdot OC_6H_4\cdot NHAc$, obtained by heating acetylorthamidophenol with phenyl cyanate in toluene, forms long, pale-red, stellate needles melting at 162°.

Phthalanilphenyl phenylcarbamate, $NHPh\cdot COO\cdot C_6H_4N<^{CO}_{CO}>C_6H_4$, is obtained when phenyl acetate is heated with hydroxyphthalanil, $HO\cdot C_6H_4N<^{CO}_{CO}>C_6H_4$ (obtained by the action of phthalic anhydride on orthamidophenol); it crystallises in beautiful, colourless needles melting at 160—165°. A. G. B.

Trinitrazoxybenzenes and Trinitrazobenzenes. By H. KLINGER and J. ZUURDEEG (*Annalen*, **255**, 310—338).—Schmidt (*Zeit. f. Chem.*, 1869, 421) has described a trinitrazoxybenzene (m. p. 152°) which he obtained by treating azoxybenzene with a mixture of sulphuric and nitric acid; according to Petriew (*ibid.*, 1870, 265) this same azoxy-compound is formed, together with a trinitroazobenzene, by heating azobenzene with concentrated nitric acid.

The authors' experiments show that Schmidt's azoxy-compound is a mixture of various substances; when azoxybenzene (20 grams) is treated with a well-cooled mixture of nitric acid of sp. gr. 1·5 (200 grams) and sulphuric acid of sp. gr. 1·8 (100 grams), and the solution kept for 24 hours, crystals are deposited. The more readily soluble crystals consist of various substances, melting below 140°, which could not be isolated; the more sparingly soluble crystals consist of a mixture of ortho- and meta-trinitrazoxybenzene which can be separated by repeated recrystallisation from benzene or acetone; the most sparingly soluble crystals melt at 207—208°, and are only formed in very small quantities.

Orthotrinitrazoxybenzene, $\overset{6}{N}O_2\cdot C_6H_4\cdot \overset{1}{N}_2O\cdot C_6H_3(NO_2)_2$ $[(NO_2)_2 = 3:4$ or $2:4]$, crystallises from acetone in well-defined, almost colourless asymmetric prisms or plates, $a:b:c = 0·79919:1:1·13901$, and melts at 187—188°; it is very sparingly soluble in ether, alcohol, and light petroleum, but rather more readily in hot chloroform, glacial acetic acid, acetone, nitrobenzene, and hot nitric acid. It is not acted on by dilute acids or dilute alkalis, but it dissolves in concentrated sulphuric acid yielding a yellowish solution from which, on cooling, it crystallises unchanged. On complete reduction with tin and hydrochloric acid in alcoholic solution, it yields a mixture of bases which probably consists of triamido- and orthodiamido-benzene.

Metatrinitrazoxybenzene, $\overset{5}{NO_2}\cdot C_6H_4\cdot \overset{1}{N_2}O\cdot C_6H_3(NO_2)_2$ [$(NO_2)_2$ = 2 : 4], crystallises from benzene in lemon-yellow, asymmetrical prisms, $a : b : c$ = 0·71085 : 1 : 0·71096, and melts at 175—176°; its behaviour with solvents is very like that of the ortho-compound, and it dissolves in concentrated sulphuric acid, yielding a yellowish solution.

Orthotrinitrazobenzene, $NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(NO_2)_2$, separates on cooling when orthotrinitrazoxybenzene (5·5 grams) is dissolved in glacial acetic acid and treated with a solution of tin (6 grams) in hydrochloric acid; it can also be prepared by reducing the azoxy-compound with alcoholic ammonium sulphide. It crystallises from glacial acetic acid, benzene, acetone, alcohol, chloroform, and nitric acid in long, yellow needles, melts at 220°, and is much more readily soluble than the azoxy-compound. It is not changed on prolonged boiling with fuming nitric acid or with a mixture of chromic acid and nitric acid. The mother-liquors obtained in the preparation of the trinitrazo-compound contain orthonitraniline and a red substance which could not be obtained in a crystalline condition.

Metatrinitrazobenzene, $NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(NO_2)_2$, is obtained when metanitrazoxybenzene (11 grams) is dissolved in boiling glacial acetic acid and treated with a solution of tin (8 grams) in concentrated hydrochloric acid; on cooling, the product separates in red plates or needles. It separates from benzene in crystals, melts at 172—173°, and resembles the corresponding ortho-compound in its behaviour with solvents; when boiled for several hours with a mixture of chromic acid and fuming nitric acid, it is reconverted into the azoxy-compound (m. p. 175—176°). The mother-liquors from the trinitrazo-compound contain metanitraniline (m. p. 114°) and a red substance which could not be obtained in crystals.

The ortho- and meta-trinitrazoxybenzene, described above, are both formed when (1) azobenzene, (2) orthonitrazoxybenzene, (3) paranitrazoxybenzene, (4) paranitrazobenzene (m p. 166—167°), and (5) dimetadinitrazobenzene are treated with nitric acid nnder suitable conditions. Janovsky and Erb (Abstr., 1885, 894) have stated that by the nitration of paranitrazobenzene there is formed a trinitrazobenzene which can also be prepared from azobenzene and from paradinitrazobenzene in like manner. The authors criticise Janovsky's results, and point out that his own statements in different journals are self-contradictory; the trinitrazobenzenes described by Janovsky are evidently mixtures of various compounds. F. S. K.

Resorcinol and Orcinol Colouring Matters. By R. Nietzki and H. Maeckler (*Ber.*, **23**, 718—726).—In continuation of their researches on the colouring matters derived from resorcinol (this vol., p. 156), the authors have re-examined the compounds obtained from the ethers of resorcinol and from orcinol (Abstr., 1881, 726; *Ber.*, **17**, 440). Weselsky and Benedikt obtained two compounds by the action of nitric acid containing nitrous acid on resorcinol monoethyl ether, to the first of which they gave the formula $C_{14}H_{11}NO_3$. The authors have been able to confirm this formula, and find that the

substance is identical with the ethyl ether of resorufin previously obtained by them (*loc. cit.*). They have, however, been unable to confirm the statement that this compound is also obtained from resorcinol diethyl ether. They have also been unable to obtain the second compound mentioned by Weselsky and Benedikt, but do not doubt its existence, as the description given by them corresponds very closely with that of resazurin ethyl ether.

The "diazoresorcinol diethyl ether" obtained by Weselsky and Benedikt by the action of alcoholic hydrogen chloride on resazurin is probably a crude resorufin ethyl ether containing chlorinated impurities.

The colouring matter from orcinol was prepared according to Weselsky's directions (*Ber.*, **17**, 440), and the analysis of the substance itself and its sodium salt confirmed the formula $C_{14}H_{11}NO_3$ given by Weselsky and by Krämer (Abstr., 1884, 1341). This formula corresponds with that of resorufin, and not with that of resazurin, and, as the colour characteristics of its alkaline solution cannot be distinguished from those of the former, it must be the next higher homologue of that substance, and the authors, therefore, propose for it the name *orcirufin*. With bromine, it yields a blue colouring matter similar to that given by resorufin, and gives an *acetyl*-derivative, $C_{14}H_{10}NO_3Ac$, crystallising in orange-needles which melt at 204°. Its *silver salt* is a dark-grey precipitate, which yields *orcirufin monethyl ether*, $C_{14}H_{10}NO_3 \cdot C_2H_5$, on warming with ethyl iodide and alcohol. This crystallises from alcohol in slender, yellowish needles melting at 269°.

The colouring matter obtained by Liebermann (Abstr., 1875, 167) by the action of sulphuric acid containing nitrous acid on orcinol, and further examined by Krämer (Abstr., 1884, 1340), consists of impure orcirufin. This may also be obtained by warming nitroso-orcinol with orcinol in sulphuric acid solution.

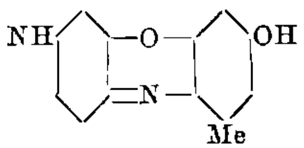
Nitroso-orcinol was obtained by Krämer by evaporating orcinol with an equivalent quantity of sodium hydroxide, mixing the product with amyl nitrite and sand, and heating the whole on the water-bath. It is, however, obtained in a much purer condition and in larger quantity by cooling the mixture with ice. It crystallises from alcohol in yellow needles which melt with a slight explosion at 157°.

Action of quinonedichlorimide on resorcinol and orcinol.—In the previous communication, the authors showed that quinonechlorimide reacts with resorcinol forming resorufin. They have now investigated the action of quinonedichlorimide on both resorcinol and orcinol, but as the yield obtained from the latter is much larger, that reaction alone has as yet been closely studied.

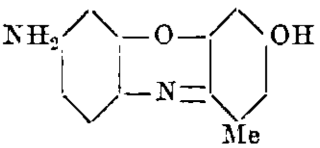
In carrying out this synthesis, an alcoholic solution of orcinol is gradually added to a similar solution of an equimolecular proportion of quinone dichlorimide, the mixture heated for several hours on the water-bath, after which water and a slight excess of ammonia is added to the carmine-red solution. The brownish-violet precipitate is taken up with alcohol containing hydrogen chloride, and dilute sulphuric acid added. On cooling, the sulphate separates as a crystalline precipitate which is insoluble in water, but may be recrys-

tallised from dilute hydrochloric acid, and is thus obtained in beautiful needles with a brown surface lustre. The *hydrochloride* is also insoluble in water, but soluble in dilute acid, which is probably due to the fact that the salts are decomposed by water. Neither of the salts mentioned contains a constant quantity of sulphuric or hydrochloric acid. The free base, obtained by the action of ammonia on a hot solution of the sulphate or hydrochloride, forms small, brown needles with a green, metallic lustre, and has the composition $C_{13}H_{10}N_2O_2$. The solutions of its salts have a colour and fluorescence which can hardly be distinguished from that of an alkaline solution of resorufin or orcirufin. In alcoholic solution, the orange fluorescence is very notable. Concentrated sulphuric acid dissolves the substance with a blue colour which passes into red on the addition of water; it dyes silk the colour of the base, but the fibres show no fluorescence.

From its mode of formation two formulæ are possible for this colouring matter, namely:—



or



The decided basic properties of the compound, its total insolubility in alcohol, and the fact that it yields only a monacetyl-derivative, all point to the latter formula as more probable. The *monacetyl* compound, $C_{13}H_9N_2O_2Ac$, is prepared by warming the base with acetic anhydride and sodium acetate, and forms stellate groups of small, brown needles; it has neither acid nor basic properties, which also agrees with the second formula. Still further confirmation of the latter is afforded by the fact that the base may be diazotised, and then condenses with naphtholsulphonic acids to azo-colours.

The colouring matter obtained in the same manner from resorcinol shows just the same colour and fluorescence, and yields salts showing the same properties as those obtained from orcinol; it must, therefore, be the simplest member of this class of colouring matters. For these two members the authors propose the names *resorufamine* and *orcirufamine*.

H. G. C.

Indulines. By O. FISCHER and E. HEPP (*Ber.*, **23**, 838—841).—Two compounds are formed when a mixture of amidoazobenzene (160 grams), aniline (400 grams), and aniline hydrochloride (320 grams) is heated to about 130°, and then for about ten minutes at 160°; the melt is treated with the theoretical quantity of sodium carbonate, the aniline distilled with steam, the residue boiled with 30 per cent. acetic acid (1·5 litres), and the filtered solution allowed to cool slowly. After a lapse of several days, the acetate of an induline of the composition $C_{24}H_{18}N_4$ separates from the solution as a bronze-coloured, crystalline precipitate and, on adding concentrated hydrochloric acid to the mother-liquors, the hydrochloride of an induline of the composition $C_{18}H_{13}N_3$ and the induline $C_{24}H_{18}N_4$ are precipitated together in a blue, amorphous condition. The free bases can be

separated by crystallisation from hot benzene, in which the compound of higher molecular weight is the more sparingly soluble.

The new induline, $C_{18}H_{13}N_3$, crystallises from benzene in green needles, melts at 135°, and is soluble in ether, benzene, and alcohol, yielding magenta-coloured solutions; its solution in acetic acid is reddish-violet, and that in concentrated sulphuric acid bluish-violet. The *hydrochloride*, $C_{18}H_{13}N_3,HCl$, the *sulphate*, and the *nitrate*, $C_{18}H_{13}N_3,HNO_3$, are readily soluble in warm water, and impart to fibres a bluish-violet colour. When the base is heated with concentrated hydrochloric acid at 150°, it is decomposed with liberation of ammonia, yielding a new dye which has probably the composition $C_{18}H_{12}N_2O$; this compound has a brownish-red fluorescence, and its solutions are of a redder shade than those of the induline.

The induline $C_{18}H_{13}N_3$ has probably the constitution

$$\overset{5}{N}H{:}C_6H_3{<}\begin{matrix}\overset{2}{N}{-}\!\!-\\ \underset{3}{N}Ph\end{matrix}{>}C_6H_4;$$

if it can be proved to be related to phenazine, the constitution of the indulines is practically settled, as all other indulines of the benzene series are derived from phenazine by the entrance of anilido-, phenyl-, or $NH_2{\cdot}C_6H_4{\cdot}N{=}$ groups.

Paraphenylenediamine reacts very readily with all indulines; it is formed in all amidoazobenzene melts in considerable quantities, but disappears again on further heating, so that it evidently takes part in the formation of the blue indulines. When paraphenylenediamine is added to the melt, the induline formation takes place at a lower temperature, and the melt becomes blue more quickly.

Indulines are readily formed when azophenine, anilidoquinoneanilide, anilidonaphthaquinoneanil, benzeneazo-α-naphthylamine, &c., are heated with paraphenylenediamine in alcoholic solution at 150—170° in presence of paraphenylenediamine hydrochloride.

The hydrochloride of a base $C_{28}H_{20}N_4$ is formed when phenylrosinduline is heated for several hours with paraphenylenediamine (2 parts) and its hydrochloride ($1\frac{1}{2}$ parts) in alcoholic solution at 160°. This salt crystallises in bronze-coloured plates, is readily soluble in alcohol, and dissolves in warm water yielding a reddish-violet solution. The free *base* crystallises from hot alcohol in dark, bronze-coloured needles, melts at 247°, and dissolves in alcohol with a dirty violet coloration; it is an amidophenylrosinduline of the constitution $NH_2{\cdot}C_6H_4{\cdot}\overset{5}{N}{:}C_6H_3{<}\begin{matrix}\overset{2}{N}{-}\!\!-\\ \underset{3}{N}Ph\end{matrix}{>}C_{10}H_6$, as, when heated with concentrated hydrochloric acid (10 parts) and a little glacial acetic acid at 180°, it is decomposed into paraphenylenediamine and rosindon (m. p. 259°).

These experiments show that the anil-group in phenylrosinduline is replaced by the atomic complex, $NH_2{\cdot}C_6H_4{\cdot}N{=}$; paraphenylenediamine has very probably an analogous action on the benzene indulines, and by the entrance of the $NH_2{\cdot}C_6H_4{\cdot}N{=}$ group into the molecule,

the shade becomes more decidedly blue, and the molecule more basic.

A complete account of these experiments will shortly be published in the *Annalen*. F. S. K.

Benzylphosphines and their Derivatives. By E. A. LETTS and R. F. BLAKE (*Trans. Roy. Soc. Edin.*, **35**, 527—628; compare also this vol., p. 492). The authors prepared monobenzylphosphine by Hofmann's method (heating 4 grams of zinc oxide, 16 grams of phosphonium iodide, and 12 grams of benzyl chloride in a sealed tube for six hours), but found that better results were obtained at 120° than at 160°. In the treatment of the products, precautions were taken to exclude the air. It was found impossible to satisfactorily purify the monobenzylphosphine by fractional distillation, but this was effected by its conversion into the hydriodide. When pure, it is a highly refractive liquid which fumes strongly when exposed to the air, becoming very hot and often inflaming spontaneously. Its *hydrobromide* is obtained by saturating a benzene solution of the base with hydrobromic acid, or by dissolving the phosphine in the fuming acid, and crystallises in scales insoluble in benzene. This salt is very deliquescent, and decomposes rapidly in contact with water, instantly with potash. The *hydrochloride* forms colourless scales, the *platinochloride* a bulky, yellow precipitate. When slowly oxidised by exposure to a limited quantity of air, the phosphine yields *benzylphosphinous, benzylphosphinic*, and phosphoric acids, the first-named in by far the largest proportion. Benzylphosphinous acid is a syrupy liquid which refuses to crystallise. It is fairly soluble in water, but separates from a strong solution in oily drops. It is easily soluble in alcohol and ether. Most of its salts are easily soluble. The *barium salt*, $(C_7H_7{\cdot}PHO_2)_2Ba + 4H_2O$, forms a granular, crystalline mass; the *calcium*, with $\frac{1}{3}H_2O$, *magnesium*, with $5H_2O$, *zinc*, and *lead*, with $\frac{1}{2}H_2O$, salts are all colourless and crystalline; the *cadmium salt* is flocculent and white. When heated, benzylphosphinous acid is decomposed into monobenzylphosphine and benzylphosphinic acid, probably according to the equation $3C_7H_7{\cdot}PH_2O_2 = 2C_7H_7{\cdot}PH_2O_3 + C_7H_7{\cdot}PH_2$. Bromine acts on benzylphosphinous acid, but the reaction seems to be very complicated.

Monobenzylphosphinic acid, $C_7H_7{\cdot}H_2PO_3$. is best obtained by the action of benzyl alcohol on a mixture of phosphorus and phosphorus iodide. It is a colourless, crystalline bibasic acid melting at 169—169·5° (corr.), and soluble in water and alcohol. Its salts mostly crystallise readily. The *barium salt*, $C_7H_7{\cdot}BaPO_3 + 2H_2O$, crystallises in thin plates much less soluble in hot than cold water: 100 c.c. water at 9·7° dissolve 1·807 grams at 100°, 0·4305 gram of the hydrated salt. The *hydrogen barium salt* $(C_7H_7{\cdot}PHO_3)_2Ba + 3H_2O$, is crystalline and very soluble. The normal *calcium*, *lead*, and *magnesium* salts are all crystalline, and contain 1 mol. H_2O, which they only lose at 200°. The *cadmium* and *zinc* salts contain 1 mol. H_2O, which they lose at 110°. The *sodium*, *potassium*, and *ammonium* salts are crystalline and very soluble; the *silver* salt forms an unstable, white precipitate. When moderately heated (at 200—230°), the

acid forms a *pyro-acid* $(C_7H_7)_2H_2P_2O_5$, yielding a *barium salt* crystallising in long needles. When heated rapidly, the normal acid decomposes, yielding metaphosphoric acid and probably toluene. When heated with phosphorous acid, benzylphosphinic acid gives off hydrogen phosphide and monobenzylphosphine, the reaction appearing to take place principally according to the equation $3H_3PO_3 + C_7H_7{\cdot}H_2PO_3 = 3H_3PO_4 + C_7H_7{\cdot}PH_2$.

When sulphur is warmed with monobenzylphosphine, hydrogen sulphide is evolved, and *pyrobenzylthiophosphinic* acid, $(C_7H_7)_2H_2P_2S_5$, is formed, which is a viscous mass, and when boiled with water, yields the thiophosphinic acid, $C_7H_7{\cdot}PS(OH)_2$, the latter forming a crystalline *barium* salt. A crystalline salt, $(C_7H_7)_2P_2S_3O_2Ba + 2H_2O$, was also obtained. Bromine acts with explosive violence on benzylphosphine, but if the action is moderated, monobenzylphosphine hydrobromide is formed. By the action of carbon bisulphide on the phosphine, two crystalline compounds were obtained, but their formulæ have not been established. Sulphuric acid appears to form with the phosphine an unstable crystalline sulphate, but this substance could not be obtained pure. When a mixture of the phosphine and chloracetic acid is heated in sealed tubes at 120°, acetic chloride and benzylphosphinic acid are formed. Bromacetic acid and ethyl chlorocarbonate both act very violently on the phosphine, but the products have not yet been isolated.

The products of Hofmann's sealed tube reaction undoubtedly contain besides mono-benzylphosphine, *di-* and *tribenzylphosphines* and *tetrabenzylphosphonium iodide.* Although they have not been able to obtain *dibenzylphosphine* in an absolutely pure state, the authors have established the fact that it is a liquid which cannot be distilled without decomposition into the mono- and tribenzylphosphines. It combines with hydriodic acid and probably other hydracids to form crystalline compounds decomposed by water. *Tribenzylphosphine* is a solid, crystalline substance of high boiling point, possibly volatile in a vacuum with little or no decomposition. It unites with hydracids to form salts which are decomposed by water, and combines energetically with benzyl iodide to form tetrabenzylphosphonium iodide. It oxidises, on exposure to air, to tribenzylphosphine oxide, which the authors have shown (*loc. cit.*) to be identical with Hofmann's dibenzylphosphine.

Numerous salts and double salts of tetrabenzylphosphonium are described.

Besides those already mentioned, the authors obtained from the sealed tube products a crystalline substance of very low boiling point ("crystalline oil"), seemingly of the formula $(C_7H_7)_2HPO$, and an "insoluble crystalline body" for which analysis seems to indicate the formula $(C_7H_7)_3PO_2$, but these formulæ are still somewhat uncertain.

Dibenzylphosphinic acid, $(C_7H_7)_2HPO_2$, was obtained amongst the products of Hofmann's sealed tube reaction, but whether formed during the reaction or during the subsequent treatment, the authors were unable to determine. It is also formed by the action of benzyl alcohol on a mixture of phosphorus and phosphorus iodide, and by fusing tribenzylphosphine oxide with caustic potash. It is fairly soluble in hot alcohol, almost insoluble in water. It crystallises in

iridescent, micaceous plates which melt at 192°. At a higher temperature it decomposes, but also partly volatilises unchanged. It forms characteristic salts. The *barium* salt, $[(C_7H_7)_2PO_2]_2Ba + 8H_2O$, and the *calcium* salt, with $8H_2O$, crystallise in thin plates, the *magnesium* salt, with $3H_2O$, in long, colourless needles. The *cadmium* salt forms a white, amorphous precipitate, the *copper salt* a blue, amorphous powder, the *silver* salt colourless needles which blacken slightly on drying. The *sodium*, *potassium*, and *ammonium* salts crystallise with 7 mols. H_2O in easily soluble crystals. Phosphorus pentachloride reacts strongly with the dibenzyl acid, but no organic compound other than benzyl chloride could be isolated, and the decomposition appears to be complete. When dibenzylphosphinic acid is heated, it is partly distilled, partly decomposed, some tribenzylphosphine oxide being formed.

When benzyl alcohol is allowed to act on a mixture of phosphorus and phosphorus iodide, all the oxidation products above described are formed, the proportions of the various products varying according to the conditions of the experiment. L. T. T.

Action of Ethyl Acetoacetate on Cinnamaldehyde. By P. BIGINELLI (*Gazzetta*, **19**, 212—214).—Hantzsch (Abstr., 1883, 82) found that the action of ethyl acetoacetate on certain aldehydes in presence of alcoholic ammonia resulted in the formation of compounds of the formula $NH{<}{\genfrac{}{}{0pt}{}{CMe{:}C(COOEt)}{CMe{:}C(COOEt)}}{>}CHR$ (compare Schiff and Puliti, Abstr., 1883, 1151). If a similar action were to take place in presence of compound ammonias, the action of ethylenediamine on cinnamaldehyde should give rise to a substance composed of two nuclei of the above form, united by ethylene through the nitrogen-atoms.

The reaction, however, does not take place in this way. When cinnamaldehyde (13·2 grams), ethyl acetoacetate (26 grams), ethylenediamine (3 grams), and absolute alcohol (10 grams) are heated for an hour in a reflux apparatus, the product, after cooling, draining, and washing with 80 per cent. alcohol, crystallises from alcohol in groups of long, silky needles which melt at 160—161° and have the composition $C_{21}H_{26}O_6$. This substance is soluble in alcohol and most ordinary solvents except water. It dissolves in acetic acid without undergoing any change. It acquires a rose colour by the action of concentrated sulphuric acid, in which it afterwards dissolves forming a greenish-yellow solution. It is decomposed by potash with the formation of a compound resembling benzoic acid in appearance and properties, but melting at 130—131°. The bromine-derivative melts at about 80°.

Methylamine or aniline may be substituted for ethylenediamine in the reaction between cinnamaldehyde and ethyl acetoacetate without affecting the composition of the product; it would, therefore, appear that ethylenediamine merely provides an alkaline menstruum in which the other substances can react.

With ethylenediamine and ethyl acetoacetate, benzaldehyde gives

a crystalline compound containing no nitrogen; propaldehyde, on the other hand, yields azotised products. S. B. A. A.

Aromatic Alkyl Ketones; their Oxidation by Potassium Permanganate. By A. Claus (*J. pr. Chem.* [2], **41**, 396—414; compare Abstr., 1885, 1136; 1886, 462, 463; 1887, 253).—Aromatic alkyl ketones can only be oxidised by potassium permanganate to ketonic acids when the benzene nucleus contains a side-group in the ortho-position to the ketone-group; and when this oxidation takes place, an α-ketonic acid is always obtained, independently of the number of carbon atoms in the alkyl-group and of this being primary or secondary.

Paratolyl methyl ketone (Abstr., 1886, 462) boils at 222° (uncorr.), not 220°, and is still liquid at −20°; its sp. gr. is 1·013 at 13°; it is slightly volatile with steam, and gives no crystalline compound with alkaline sulphites. If the action of the aluminium chloride is prolonged, a thick, yellow oil boiling above 300° is formed; it seems to be a condensation-product.

Paratolyl dibromomethyl ketone, obtained by adding bromine to a solution of the ketone in carbon bisulphide, crystallises in beautiful, colourless leaflets, which are sparingly soluble in alcohol; it melts at 97° (uncorr.), and does not sublime; it yields toluic and terephthalic acids when oxidised, but no ketonic acid. When this dibromo-derivative is treated with alcoholic potash, it yields *tolyl ketone aldehyde*, $C_6H_4Me·CO·CHO$, or a polymeride thereof; this substance crystallises in nodular aggregates which melt at 170° (uncorr.) and sublime in colourless needles.

Paratolyl methyl acetoxime, $C_6H_4Me·CMe:N·OH$, crystallises in colourless, six-sided tables melting at 88° and insoluble in water, but soluble in alcohol, ether, and chloroform. *Paratolyl methyl ketone phenylhydrazide* crystallises in lustrous, colourless prisms melting at 95° (uncorr.).

Paratolyl methyl pinacone, $C_6H_4Me·CMe(OH)·CMe(OH)·C_6H_4Me$, is prepared by adding sodium amalgam (5 per cent.) in small quantities to a solution of the ketone in 70 per cent. alcohol (10 vols.); when the solution has become colourless, it is acidified with dilute sulphuric acid and mixed with much water; the pinacone separates as a yellow oil which crystallises from alcohol in large, hexagonal tables, melts at 90° (uncorr.), and is soluble in ether and chloroform. When the pinacone is reduced with potash and zinc, *paratolyl methyl carbinol*, $C_6H_4Me·CHMe·OH$, a yellow oil boiling above 300°, is obtained.

When paratolyl methyl ketone is warmed with sulphuric acid, it undergoes condensation forming a *phorone*, $C_{27}H_{26}O$, which crystallises in lustrous, colourless needles melting at 168°; it is insoluble in water, sublimes easily, and burns with a bright, luminous flame. This substance is under investigation.

Tritolylbenzene, $C_6H_3(C_7H_7)_3$, is obtained when dry hydrogen chloride is passed into paratolyl methyl ketone daily for two weeks; the brown mass is washed with alcohol and crystallised from chloroform, from which the tritolylbenzene crystallises in white needles, whilst from alcohol and acetone, it crystallises in leaflets; both forms melt at 171° (uncorr.) and decompose at 220°, but do not sublime.

Tribromotritolylbenzene crystallises in colourless, felted needles which melt at 212° (uncorr.). *Trinitrotritolylbenzene* separates from the usual solvents as a crystalline powder; it begins to decompose at 160°, and does not melt.

Benzenetribenzoic acid, $C_6H_3(C_6H_4 \cdot COOH)_3$, is obtained by heating tritolylbenzene with dilute nitric acid of sp. gr. 1·1 (5—6 parts) at 160—180° in a sealed tube. It separates from alcohol as a nearly colourless, crystalline powder sparingly soluble in ether and chloroform, insoluble in water; it sublimes in needles, without melting, at 280°. The *normal*, *monacid*, and *diacid potassium* salts and the *normal ammonium* salt were obtained.

Ortho-xylyl methyl ketone is a mobile, colourless, strongly refractive, oily liquid; it boils at 243° (uncorr.), and is soluble in the usual solvents, except water. Its *oxime* crystallises from ether in colourless, lustrous, flat needles and prisms melting at 89—90° (uncorr.). Its *phenylhydrazide* forms colourless crystals melting at 113° (uncorr.).

Ortho-xylyl methyl carbinol, obtained by reducing the ketone with zinc-dust in alcoholic potash, is a clear, yellowish liquid of pleasant odour, and boils between 255° and 260° (uncorr.). When reduced with hydriodic acid, it yields 1 : 2-dimethyl-4-ethylbenzene.

When ortho-xylyl methyl ketone is oxidised with potassium permanganate, it yields only metaparadimethylbenzoic acid (paraxylic acid; m. p. 163°). When it is treated with dry hydrogen chloride, the compound $C_{20}H_{22}O$ is obtained; this crystallises in nearly colourless needles, melts at 113° (uncorr.), and is soluble in ether and sparingly in alcohol, but insoluble in water. In one experiment, a small quantity of a second substance, melting at 173° (uncorr.), was obtained. Attempts to bring about a condensation of the ketone by phosphoric anhydride led to the formation of metaparadimethylbenzoic acid (m. p. 163°).

Ortho-cymyl methyl ketone is a liquid boiling at 256—260° (uncorr.); it yields 4-methylisophthalic acid when oxidised, but no ketonic acid.

A. G. B.

Anisaldehyde and Succinic Acid. By R. FITTIG and J. POLITIS (*Annalen*, **255**, 293—309; compare this vol., pp. 583—594).—*Anisylisocrotonic acid*, $OMe \cdot C_6H_4 \cdot CH{:}CH \cdot CH_2 \cdot COOH$, is formed, together with dianisylpentolic acid and dianisyltetrylene, when anisaldehyde is heated at 120° for 30 to 40 hours with sodium succinate and acetic anhydride. The dark-brown product is treated with sodium carbonate, the alkaline solution extracted with ether, filtered from the impure dianisyltetrylene, and acidified strongly with hydrochloric acid, whereon anisylisocrotonic acid and dianisylpentolic acid are precipitated, and can be easily separated by treating the mixture with hot water, in which the former alone is soluble.

Anisylisocrotonic acid separates from water in colourless plates, melts at 106·5°, and is readily soluble in ether, alcohol, and chloroform, and moderately easily in hot water, but only sparingly in carbon bisulphide, and very sparingly in cold water. It is isomeric with the paramethoxyphenylcrotonic acid obtained by Perkin (Trans., 1877, 411) from anisaldehyde and propionic acid. The *barium* salt, $(C_{11}H_{11}O_3)_2Ba + 3H_2O$, crystallises from hot water in plates, and is

only moderately easily soluble in cold water; the *calcium* salt, with $2H_2O$, crystallises from water in needles, and is more sparingly soluble than the barium salt; the *silver* salt, $C_{11}H_{11}O_3Ag$, is only sparingly soluble in boiling water. The acid is not reduced by sodium amalgam; it combines with concentrated hydrobromic acid at 0°, yielding a crystalline compound which is very unstable.

Anisylbromobutyrolactone, $OMe{\cdot}C_6H_4{\cdot}CH<\begin{matrix}CHBr{\cdot}CH_2\\ O\text{——}CO\end{matrix}$, can be prepared by treating anisylisocrotonic acid with bromine (1 mol.) in cold carbon bisulphide solution, and keeping the crystalline dibromo-acid, $C_{11}H_{12}Br_2O_3$, thus produced for a few days; as soon as the evolution of hydrogen bromide is at an end, the lactone is recrystallised from chloroform or glacial acetic acid, from which it separates in well-defined, monosymmetric crystals, $a : b : c = 1{\cdot}6554 : 1 : 0{\cdot}5997$, $\beta = 85° 56'$, melting at 118·5°.

Anisylbutyrolactone, $OMe{\cdot}C_6H_4{\cdot}CH<\begin{matrix}CH_2{\cdot}CH_2\\ O\text{—}CO\end{matrix}$, prepared by reducing the preceding compound with sodium amalgam in cold alcoholic glacial acetic acid solution, crystallises from boiling water in plates, melts at 53·5°, and is readily soluble in ether, carbon bisulphide, and chloroform, but only very sparingly in light petroleum, and insoluble in sodium carbonate; it has a slight aromatic odour, and is only very slightly volatile with steam.

Barium anisylhydroxybutyrate is obtained when the lactone is boiled with a solution of barium hydroxide; it is a brittle, amorphous compound moderately easily soluble in water and alcohol. When an aqueous solution of the barium salt is acidified, extracted with ether, and the ethereal solution evaporated, the hydroxy-acid remains as a solid, colourless mass; it melts at about 80°, probably with decomposition, and is completely reconverted into the lactone on warming with dilute hydrochloric acid.

Dianisylpentolic acid, $OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C(COOH){:}CH{\cdot}C_6H_4{\cdot}OMe$ (see above), crystallises from glacial acetic acid in long, yellow needles, melts at 160°, and is almost insoluble in water and only very sparingly soluble in carbon bisulphide, but moderately easily in alcohol, ether, chloroform, and benzene. The *barium* salt $(C_{19}H_{17}O_4)_2Ba + 2H_2O$ crystallises from hot, dilute alcohol in colourless plates, and is almost insoluble in water; the anhydrous salt is yellow. The *calcium* salt, with $3H_2O$, resembles the barium salt; the *silver* salt, $C_{19}H_{17}O_4Ag$, is almost insoluble in water. Dianisylpentolic acid does not combine with concentrated hydrobromic acid at 0°; when treated with bromine (2 mols.) in chloroform solution, hydrogen bromide is evolved, and a compound of the composition $C_{19}H_{17}Br_3O_4$ is obtained. This substance melts at 140° with decomposition, and is doubtless a brominated lactone.

Dianisylpentylenic acid,

$$OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH(COOH){\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe,$$

is obtained by reducing the pentolic acid with sodium amalgam in alkaline solution. It crystallises from benzene with 1 mol. of ben-

zene, and from carbon bisulphide in colourless needles melting at 111°; it is readily soluble in alcohol, ether, and benzene, but only sparingly in carbon bisulphide, light petroleum, and water. The *calcium* salt, $(C_{19}H_{19}O_4)_2Ca + 2H_2O$, is almost insoluble in water, and is not easily obtained in crystals; the *silver* salt, $C_{19}H_{19}O_4Ag$, is almost insoluble in water.

Dianisylbromopentalactone,

$$OMe{\cdot}C_6H_4{\cdot}CH<\genfrac{}{}{0pt}{}{CHBr}{O-CO}>CH{\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe,$$

is obtained by treating dianisylpentylenic acid with bromine in cold carbon bisulphide solution, and dissolving the impure dianisyldibromovaleric acid, $C_{19}H_{20}Br_2O_4$, thus produced, in glacial acetic acid. It crystallises in colourless needles, melts at 136°, and is insoluble in cold alkaline carbonates.

Dianisylpentalactone, $OMe{\cdot}C_6H_4{\cdot}CH<\genfrac{}{}{0pt}{}{CH_2-}{O{\cdot}CO}>CH{\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe$, prepared by treating the bromo-lactone with sodium amalgam in acetic acid solution, separates from acetic acid in small, prismatic crystals, melts at 83°, and is readily soluble in ether, chloroform, and carbon bisulphide, but insoluble in sodium carbonate.

Barium dianisylhydroxyvalerate is obtained as a gummy mass by boiling the lactone with baryta-water; when decomposed with acids, it yields the hydroxy-acid as a colourless, crystalline compound.

Dianisyltetrylene, $OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OMe$, is obtained in a pure condition by washing the impure residue referred to above with warm water; it separates from benzene in colourless crystals with a violet fluorescence, and is almost insoluble in water, alcohol, and ether, and only sparingly soluble in carbon bisulphide, but more readily in glacial acetic acid, chloroform, and benzene. It sinters together at 225°, and does not melt completely until 235—238°. This compound can also be obtained by distilling dianisylpentolic acid with lime; when boiled with potassium permanganate, it yields anisic acid. The *tetrabromide*, $C_{18}H_{18}Br_4O_2$, is a colourless, crystalline compound very sparingly soluble in carbon bisulphide, more readily in chloroform; it is decomposed by boiling chloroform, or when heated alone, with evolution of hydrogen bromide. F. S. K.

Action of Ethyl Sodacetoacetate on Tribromodinitrobenzene. By C. L. JACKSON and G. D. MOORE (*Amer. Chem. J.*, **12**, 164—181; compare Abstr., 1889, 781).—Details are first given of a slightly improved method of preparing tribromodinitrobenzene from aniline, by means of which a nearly quantitative yield was obtained.

Ethyl bromodinitrophenylacetoacetate,

$$C_6H_2Br(NO_2)_2{\cdot}CH(COMe){\cdot}COOEt,$$

was prepared by adding an alcoholic solution of ethyl sodacetoacetate (about 4 mols.) to a solution of tribromodinitrobenzene (1 mol.) in benzene. The mixture was heated for an hour on the steam-bath, and then mixed with water; the reddish benzene solution which was precipitated was removed from the dark-red aqueous

solution, and the latter was made slightly acid with sulphuric acid in order to decompose the sodium salt of the new substance. This separated as a yellowish oil which was extracted with ether, and left, after evaporation of the ether, a dark, reddish-brown oil, which solidified to a mass of crystals. These were freed from adhering red oil by washing with alcohol, and were then recrystallised from this solvent. A further quantity was obtained from the benzene solution, but the average yield was only about 50 per cent. of the theoretical; probably much of the substance remained dissolved in the red oil. From the analogous reaction of tribromodinitrobenzene with ethyl sodiomalonate (compare this vol., p. 377), it is shown that ethyl bromodinitrophenylacetoacetate must have the formula given above, and not $C_6HBr(NO_2)_2\!:\!C(COMe)\cdot COOEt$. It is yellow, and crystallises in acute rhombohedra, or in prisms which show a tendency to twin. It melts at 96°, and dissolves in most solvents except water and light petroleum; hot alcohol is the best solvent. It has marked acid properties, giving red solutions with aqueous ammonia, soda, or potash; the sodium salt was obtained as a brick-red, amorphous mass; salts of the heavy metals formed yellow or reddish precipitates.

Bromodinitrobenzyl methyl ketone, $C_6H_2Br(NO_2)_2\cdot CH_2\cdot COMe$, was prepared by boiling ethyl bromodinitrophenylacetoacetate for an hour in a reflux apparatus with sulphuric acid (of sp. gr. 1·44 and boiling point 132°), and purifying the white precipitate which separated on cooling by crystallisation from alcohol. It can also be prepared, although less advantageously, by heating the ethereal salt at 130—150° with hydrochloric acid in a sealed tube. No bromodinitrophenylacetic acid is formed. The ketone crystallises from alcohol in white, rectangular plates or in tufts of needles, melts at 112—113°, and is soluble in the usual solvents, water and light petroleum excepted. It has well-marked acid properties, and gives with aqueous soda or ammonia a red solution, the colour of which is intensified by the addition of alcohol.

Anilidodinitrobenzyl methyl ketone, $NHPh\cdot C_6H_2(NO_2)_2\cdot CH_2\cdot COMe$, was prepared by warming a mixture of aniline (2 mols.) with bromodinitrobenzyl methyl ketone (1 mol.), washing the product with water, and crystallising from alcohol. It forms bright-yellow groups of curved needles melting at 131°, and dissolves in most solvents except light petroleum; its aqueous solution has a yellow colour. It has somewhat feeble acid properties, and gives with soda a brownish-red solution, but only if alcohol is present; the sodium salt was obtained as a brownish-black mass; its alcoholic solution is much browner than that of the other salts mentioned in this paper.

Anilidodinitrobenzyl methyl ketone hydrazone,

$$NHPh\cdot C_6H_2(NO_2)_2\cdot CH_2\cdot CMe\!:\!N_2HPh,$$

was made by warming anilidodinitrobenzyl methyl ketone with excess of phenylhydrazine. A tarry mass was obtained which was crystallised from alcohol, washed free from excess of phenylhydrazine with very dilute hydrochloric acid, and boiled with alcohol, enough benzene being then added to effect solution; on cooling, crystals were

deposited, and were purified by recrystallisation. It forms reddish-brown scales (resembling officinal ferric citrate) which melt at 140°, and dissolve in many solvents, but not to any extent in light petroleum, water, or ether. It has no acid properties. C. F. B.

Lactam-formation in the Fatty Series; Identity of Citraconanil and Pyranilpyroïnlactone. By R. ANSCHÜTZ (*Ber.*, **23**, 887—896).—β-Anilidopyrotartaric acid is best prepared by treating the additive compound of ethyl acetoacetate and hydrogen cyanide with aniline in ethereal solution, and keeping for three to four weeks at the ordinary temperature (compare Schiller-Wechsler, Abstr., 1885, 900); the ether is then separated and the product treated with concentrated sulphuric acid. 85 grams of ethyl anilidopyrotartramate is obtained in this way from 100 grams of ethyl acetoacetate, and the ethereal salt, on hydrolysis, yields β-anilidopyrotartaric acid, which separates from water in anhydrous, prismatic crystals, or in crystals containing 1 mol. H_2O, according to the conditions under which crystallisation takes place. When the acid is heated at 180° in sealed tubes, or distilled under a pressure of 12 mm., it is converted into citraconanil (m. p. 98°) which is identical with Reissert's pyranilpyroïnlactone in all respects. When the citraconanil, obtained in this way, is dissolved in warm baryta-water, it is converted into mesaconanilic acid.

When β-anilidopyrotartaric acid is treated with acetic chloride, it is converted into a compound melting at 136°, which seems to be the anhydride. F. S. K.

Benzylsuccinic Acid and its Homologues. By C. A. BISCHOFF and N. MINTZ (*Ber.*, **23**, 653—656).—*Ethyl benzylethenyltricarboxylate*, $COOEt\cdot CH_2\cdot C(C_7H_7)(COOEt)_2$, can be prepared from ethyl sodioethenyltricarboxylate and benzyl chloride; it boils at 336·3° (corr.) (at 230—238°; 38 mm.), and, on hydrolysis, yields benzylethenyltricarboxylic acid which melts at 168·5° with evolution of gas, being converted into benzylsuccinic acid (m. p. 161°).

Ethyl benzylpropenyltricarboxylate,

$$COOEt\cdot CHMe\cdot C(C_7H_7)(COOEt)_2,$$

prepared from ethyl sodiopropenyltricarboxylate and benzyl chloride, boils at 337·8° (corr.) and, on hydrolysis, yields a mixture of benzylmethylsuccinic acid (m. p. about 135°) and benzylpropenyltricarboxylic acid. Benzylmethylsuccinic anhydride, prepared by distilling the acid, is a crystalline compound melting at 110°.

Ethyl benzylbutenyltricarboxylate, $COOEt\cdot CHEt\cdot C(C_7H_7)(COOEt)_2$, prepared from ethyl sodiobutenyltricarboxylate in like manner, boils at 336·1° (corr.), and, on hydrolysis, gives symmetrical parabenzylethylsuccinic acid (m. p. 157·5°) and symmetrical mesobenzylethylsuccinic acid (m. p. 123·5°).

Ethyl benzylisobutenyltricarboxylate,

$$COOEt\cdot CMe_2\cdot C(C_7H_7)(COOEt)_2,$$

prepared from ethyl sodioisobutenyltricarboxylate and benzyl chloride,

boils at 336·6° (corr.), and on hydrolysis yields benzyldimethylethenyltricarboxylate together with small quantities of benzyldimethylsuccinic acid (m. p. 153—155°) and an acid of lower melting point, probably the dynamical isomeride. F. S. K.

Benzaldehyde and Pyrotartaric Acid. By R. FITTIG and L. LIEBMANN (*Annalen*, **255**, 257—275; compare this vol. pp. 583—594, and Penfield, Abstr., 1883, 473).—Two isomeric methylphenylparaconic acids are formed when benzaldehyde is heated with sodium pyrotartrate and acetic anhydride for 20 hours at 100°. The product is treated with warm water, the solution rendered alkaline with soda, extracted with ether to free it from benzaldehyde and resinous products, then concentrated by evaporation, and strongly acidified. The precipitated acids are separated, dried, dissolved in chloroform, and the insoluble pyrotartaric acid separated by filtration; the chloroform solution is then evaporated, the residue digested with hot carbon bisulphide, which removes traces of impurities, and then recrystallised from 80 per cent. alcohol, in which the α-acid is more sparingly soluble than the β-compound.

α-Methylphenylparaconic acid, $CO<\begin{matrix} O \text{——} CHPh \\ CHMe{\cdot}\overset{|}{C}H{\cdot}COOH \end{matrix}$, forms monoclinic crystals, $a : b : c = 1{\cdot}080 : 1 : 1{\cdot}082$, $\beta = 65° 26'$, and melts at 177°. The *barium* salt, $(C_{12}H_{11}O_4)_2Ba + H_2O$, is prepared by treating an aqueous solution of the acid with barium carbonate in the cold. It forms small crystals, and is moderately easily soluble in water. The *calcium* salt, with H_2O, resembles the barium salt. The free acid is not acted on by fuming hydrobromic acid, as stated by Penfield. On distillation, α-methylphenylparaconic acid gives benzaldehyde, phenylbutylene, α-methylphenylisocrotonic acid, methylnaphthol, and traces of a lactone, but a considerable quantity of the acid passes over unchanged; the distillation-products are separated as follows:—The distillate is rendered alkaline with sodium carbonate, the neutral compounds extracted with ether, the residual solution acidified, and the precipitated acids extracted with ether; the acid mixture is then distilled with water, whereon α-methylphenylisocrotonic acid passes over, whilst the unchanged paraconic acid remains.

α-Methylphenylisocrotonic acid, CHPh:CH·CHMe·COOH, crystallises from boiling water in large, indented plates, melts at 110·5°, and is readily soluble in alcohol, ether, and carbon bisulphide. The *barium* salt, $(C_{11}H_{11}O_2)_2Ba + H_2O$, is very readily soluble in cold water, from which it separates in colourless needles. When the acid is treated with concentrated hydrobromic acid at 0°, it yields an oil, which is probably impure phenylbromohydrotiglic acid, as it dissolves in cold sodium carbonate, and, on warming, the solution becomes turbid owing to the separation of an oily lactone.

Methylnaphthol is obtained by repeatedly shaking the ethereal extract (see above) with dilute soda, saturating the alkaline solution with carbonic anhydride, and recrystallising the precipitated methylnaphthol from hot water. It crystallises in long yellow needles, melts at 89°, and is very sparingly soluble in water. It gives with

ferric chloride a colourless precipitate which, on keeping, gradually turns yellow, and with a solution of bleaching powder, a very characteristic green precipitate which quickly turns yellow. When distilled with zinc-dust, it yields β-methylnaphthalene (m. p. 37—38°) identical with the compound obtained from β-methylphenylparaconic acid (see below) in like manner.

β-Methylphenylparaconic acid, $CO<\begin{matrix} O—CHPh \\ CH_2·CMe·COOH \end{matrix}$, separates from dilute alcohol in monoclinic crystals, $a : b : c = 1·278 : 1 : 1·2345$, $\beta = 82° 15'$, and melts at 124·5°. The *barium* salt, prepared in the cold, separates from water in anhydrous crystals. The *calcium* salt ($+ 2H_2O$) crystallises in needles and is readily soluble in water. The *silver* salt is readily soluble in warm water, and is very stable.

Barium β-methylphenylitamalate, $C_{12}H_{12}O_5Ba$, prepared by boiling the lactone acid with baryta-water, crystallises from water, in which it is moderately easily soluble, in small plates. The *calcium* salt, with H_2O, resembles the barium salt. The *silver* salt ($C_{12}H_{12}O_5Ag_2$) is amorphous and less stable than the corresponding salt of the lactone acid.

β-Methylphenylparaconic acid combines with concentrated hydrobromic acid at 0°, yielding a crystalline compound which melts at 149° with decomposition, and has the composition $C_{12}H_{13}BrO_4$; this compound is doubtless identical with the bromo-acid described by Penfield (*loc. cit.*), who erroneously considered it to be a derivative of the α-lactone acid; when warmed with water, it is decomposed with evolution of carbonic anhydride, yielding β-methylphenylparaconic acid and β-methylphenylisocrotonic acid. When β-methylphenylparaconic acid is distilled, it yields phenylbutylene, β-methylphenylisocrotonic acid, benzaldehyde, a methylnaphthol, and small quantities of a lactone, but a considerable quantity of the acid passes over unchanged.

β-Methylphenylisocrotonic acid, CHPh:CMe·CH_2·COOH, crystallises from hot water in colourless plates, melts at 112—113°, and is readily soluble in alcohol, ether, benzene, and carbon bisulphide, but only sparingly in boiling water. The *barium* salt, $(C_{11}H_{11}O_2)_2Ba$, crystallises from water, in which it is moderately easily soluble, in slender, anhydrous needles.

Phenylbromisovaleric acid, CHPhBr·CHMe·CH_2·COOH, was obtained as an oil by treating the preceding compound with concentrated hydrobromic acid at 0°; it dissolves in cold sodium carbonate, but, on warming, the solution becomes turbid owing to the separation of *phenylisovalerolactone*, $CO<\begin{matrix} O—CHPh \\ CH_2·CHMe \end{matrix}$.

Barium phenylhydroxyvalerate, $(C_{11}H_{13}O_3)_2Ba$, is obtained as a syrup when the lactone is boiled with baryta-water.

β-Methyl-α-naphthol, $C_{11}H_{10}O$, crystallises from boiling water in colourless needles, melts at 92°, and is readily volatile with steam; it gives the same reaction with ferric chloride and with a solution of bleaching powder as the methylnaphthol obtained from α-methylphenylparaconic acid. When distilled with zinc-dust, it yields methyl-

naphthalene (m. p. 37—38°) identical with the compound (m. p. 32·5°) described by Schulze (Abstr., 1884, 1185).

Phenylbutylene, $C_{10}H_{12}$, is a colourless oil boiling at 181° (thermometer entirely in vapour); it combines with bromine yielding a yellowish, oily dibromide, $C_{10}H_{12}Br_2$. This hydrocarbon is probably identical with the compound prepared from benzaldehyde and isobutyric acid (Perkin, Trans., 1877, 660), and also with that obtained from phenylhydroxypivalinic acid by Fittig and Jayne (Abstr., 1883, 471; 1885, 663). F. S. K.

Salicylaldehyde and Pyrotartaric Acid. By R. FITTIG and H. C. BROWN (*Annalen*, **255**, 285—292; compare preceding abstract).

—*Coumarinpropionic acid*, $C_6H_4<\begin{matrix}O-CO\\ CH:\overset{|}{C}\cdot CHMe\cdot COOH\end{matrix}$, is formed, together with orthohydroxyphenylmethylisocrotonic acid (see below), when salicylaldehyde is heated at 120° for 20 to 30 hours with sodium pyrotartrate and acetic anhydride. The mixture is treated with water, the products extracted with ether, and submitted to distillation with steam in order to get rid of the salicylaldehyde. The residual solution is evaporated to dryness to expel the acetic acid, dissolved in warm sodium carbonate, the filtered solution acidified with hydrochloric acid, and the precipitated acids extracted with ether; after evaporating the ether, an oil remains from which the coumarinpropionic acid gradually separates in crystals, whilst the hydroxyphenylmethylisocrotonic acid remains in a liquid condition.

Coumarinpropionic acid crystallises from boiling water in colourless plates, melts at 171°, and is very readily soluble in chloroform, but only sparingly in ether and cold water, and almost insoluble in benzene. The *barium* salt, $(C_{12}H_9O_4)_2Ba + 3H_2O$, is obtained by boiling an aqueous solution of the acid with barium carbonate; it forms colourless crystals, and is readily soluble in water. The *calcium* salt, with $5H_2O$, is a crystalline compound readily soluble in water. The *silver* salt, $C_{12}H_9O_4Ag$, is moderately easily soluble in water, and very stable.

Ethylcoumarin, $C_6H_4<\begin{matrix}O-CO\\ CH:\overset{|}{C}Et\end{matrix}$, is formed, with evolution of carbonic anhydride, when coumarinpropionic acid is distilled; it melts at 70—71°, and is identical with the butyrocoumarin prepared by Perkin (Trans., 1881, 439) from salicylaldehyde and butyric acid.

Orthohydroxyphenyldimethylsuccinic acid,

$$OH\cdot C_6H_4\cdot CH_2\cdot CH(COOH)\cdot CHMe\cdot COOH,$$

is obtained when coumarinpropionic acid is reduced with sodium amalgam in warm aqueous solution, the solution being kept as neutral as possible; it crystallises well from water, and melts at 145—150°, being converted into the anhydride (or lactone). It is readily soluble in water, alcohol, ether, and chloroform, but only sparingly in carbon bisulphide and benzene, and almost insoluble in light petroleum. The *anhydride* (or *lactone*), $C_{12}H_{12}O_4$, is formed when the acid is heated at 120°; it is gradually decomposed by water. The *barium* salt,

$C_{12}H_{12}O_5Ba$, prepared by neutralising the acid with barium carbonate, is amorphous, and is very readily soluble in water, but insoluble in alcohol; the *calcium* salt, $C_{12}H_{12}O_5Ca$, and the *silver* salt, $C_{12}H_{12}O_5Ag_2$, are also amorphous.

Orthohydroxyphenylmethylisocrotonic acid, $C_{11}H_{12}O_3$, is obtained in a pure condition by means of the crystalline barium salt. It separates from carbon bisulphide and from a mixture of benzene and light petroleum in large plates, melts at 73°, and is very readily soluble in chloroform and benzene, but only moderately easily in carbon bisulphide, and almost insoluble in light petroleum; when treated with a little water, it deliquesces to a colourless oil, but does not dissolve to any appreciable extent. The *barium* salt, $(C_{11}H_{11}O_3)_2Ba + 4H_2O$, crystallises in needles, and is very readily soluble in water, but insoluble in alcohol. The *calcium* salt, $(C_{11}H_{11}O_3)_2Ca$, is a syrup, very readily soluble in both water and alcohol. The *silver* salt, $C_{11}H_{11}O_3Ag$, is only sparingly soluble in, and is decomposed by, boiling water.

F. S. K.

Acids Obtained by Heating Metahydrazobenzoic Acid with Stannous Chloride. By R. Kusserow (*Ber.*, 23, 912—918).—When metahydrazobenzoic acid (1 mol.) is warmed for a long time with stannous chloride (1 mol.) in aqueous solution, it is almost completely converted into diamidodiphenic acid, which passes into solution, but a small quantity of an insoluble substance containing tin remains. When this residue is boiled with sodium carbonate, and the filtered solution allowed to cool, a sparingly soluble sodium salt separates in colourless needles, and the mother liquors contain the sodium salt of another acid. The acid obtained from 300 grams of nitrobenzoic acid yields 35 grams of the mixed sodium salts.

The *acid* $C_{14}H_{12}N_2O_4$ separates in lemon-yellow needles when a solution of the sparingly soluble sodium salt is decomposed with hydrogen sulphide; it melts above 290°, and is almost insoluble in water and alcohol. The *sodium* salt, $C_{14}H_{11}N_2O_4Na + 4H_2O$, loses its water at 180°, and is moderately easily soluble in hot, but only sparingly in cold water. The *potassium* salt crystallises in colourless needles, and seems to be rather more readily soluble than the sodium salt. The *barium* salt, $(C_{14}H_{11}N_2O_4)_2Ba + 2H_2O$, crystallises in yellowish, microscopic needles, loses its water, and becomes colourless at 200°, and is almost insoluble in water. The *silver* salt is almost insoluble in hot water, and darkens when exposed to light in a moist condition. The *hydrochloride*, $C_{14}H_{12}N_2O_4,HCl$, *hydrobromide*, and *hydriodide* crystallise in colourless, microscopic needles, and are decomposed by water. The *sulphate*, $(C_{14}H_{12}N_2O_4)_2,H_2SO_4$, crystallises in small, colourless needles, and is decomposed by boiling water. The acid is not changed on prolonged boiling with soda or by concentrated hydriodic acid at 170°. The *diazo*-compound is a light-brown, unstable, crystalline powder which is decomposed on warming with water or alcohol. The *hydrazine*-derivative, prepared by reducing the diazo-compound with stannous chloride, is a colourless, amorphous substance very sparingly soluble in boiling water, and insoluble in alcohol.

The *acid* $C_{14}H_{10}N_2O_3$ is obtained when the mother liquors from the

sparingly soluble sodium salt (see above) are evaporated, and the crystalline sodium salt decomposed with hydrochloric acid; it crystallises from hot water in needles, and does not melt when heated on platinum foil. The *barium* salt, $(C_{14}H_9N_2O_3)_2Ba + 9H_2O$?, crystallises in needles, and is very sparingly soluble in water. The *silver* salt is very sparingly soluble in water, and darkens when exposed to light in a moist condition. The salts are not decomposed by hydrogen sulphide, and their solutions show a blue fluorescence. The *hydrochloride*, $C_{14}H_{10}N_2O_3,HCl$, crystallises in microscopic needles, and is decomposed by water. The *diazo*-compound seems to be moderately stable. F. S. K.

Sulphonic Derivatives of Parapropylmetachlorotoluene. By G. Carrara (*Gazzetta*, **19**, 169—175).—The following experiments were made with a view of preparing the thiosulpho- and thiochloro-derivatives of cymene by fusing the chlorosulphonic acids with potassium sulphide.

Chlorocymene prepared from thymol and phosphoric chloride by Fileti and Crosa's method is converted into the sulphonic acid by Paterno and Canzoneri's method. Chlorhydrin sulphate (48·5 grams) is gradually added to chlorocymene (70 grams), and heated on the water-bath until no more hydrogen chloride is evolved, the residue, which consists of a yellowish oil and a white crystalline mass, is treated with 98 per cent. alcohol, by which the former is completely dissolved out. The insoluble part crystallises from 98—99 per cent. alcohol or from ether in prisms which melt at 64°, and volatilise with partial decomposition at 197°. It is insoluble in water or in a 20 per cent. solution of potash, only very sparingly soluble in cold alcohol, and moderately in absolute alcohol and ether. It has the composition $C_{10}H_{12}Cl_2SO_2$. On neutralising the aqueous extract mentioned above with barium carbonate, and submitting the barium compounds to fractional crystallisation, a salt which has the composition $(C_{10}H_{12}Cl\cdot SO_3)_2Ba + 3Aq$ is obtained as a uniform mixture of oblique prisms and rhomboidal tables. It is soluble in dilute alcohol, and very sparingly in water. The lead salt forms lustrous, nacreous plates containing 3 mols. H_2O. It is soluble in dilute alcohol, and very sparingly in water. The silver salt forms white prisms containing $\frac{1}{2}$ mol. H_2O. On exposure to light, they are first turned red, and subsequently blackened. It is soluble in water.

Chlorocymenesulphonic acid, $C_{10}H_{12}Cl\cdot SO_3H + 3Aq$.—On decomposing the lead or barium salts, separating the metals, and evaporating the residual solutions to dryness, the acid is obtained as a crystalline mass consisting of small, white prisms. If the solution is concentrated to a syrup, and left for a few days at a temperature of about 4°, it separates out in large, colourless, transparent, oblique prisms. It becomes anhydrous when exposed over sulphuric acid in a vacuum, but again takes up the 3 mols. H_2O on exposure to the air for a short time. It melts at 24° when hydrated, and at 79° when anhydrous; it turns brown when heated above 110°. It is freely soluble in water, alcohol, ether, benzene, and hot carbon bisulphide.

Nitro-derivative.—The silver salt of this compound is obtained by

evaporating a mixture of the sulphonic acid with nitric acid (sp. gr. = 1·38) to dryness three times in succession, heating with water to expel the nitric acid, neutralising with silver carbonate, and fractionally crystallising. The portion which separates out first contains lustrous, yellow needles of silver nitrochlorocymenesulphonate, $C_{10}H_{11}(NO_2)Cl·SO_3Ag + H_2O$. S. B. A. A.

Preparation of Sulphones. By R. OTTO and A. RÖSSING (*Ber.*, **23**, 752—759).—It has previously been shown by R. and W. Otto (Abstr., 1888, 282) that the mono-haloïd substitution-products of ketones are readily converted by the action of the salts of sulphinic acids into sulphoneketones, according to the equation

$$CH_2Cl·CO·CH_3 + SO_2PhNa = NaCl + SO_2Ph·CH_2·CO·CH_3.$$

If the monobromo-derivative of the phenylsulphonacetone thus obtained be further treated with sodium benzenesulphinate, it is converted into sodium chloride and symmetrical diphenylsulphonacetone, $SO_2Ph·CH_2·CO·CH_2·SO_2Ph$.

The authors have endeavoured to find other methods of preparing sulphoneketones, but obtained only negative results from the action of chloracetone on methylphenylsulphone, of benzenesulphonic chloride on acetone, and of benzenesulphonic acid and acetone in presence of phosphoric anhydride, and of acetic chloride and chloracetone on ethyl sodiophenylsulphonacetate. From ethyl chloracetate and sodium benzenesulphonate, phenylsulphonacetic acid was obtained, the acetyl-group being eliminated as acetic acid.

Positive results were, however, obtained by replacing hydrogen in ketones by a mercaptan residue, and oxidising the compound thus formed with potassium permanganate. Chloracetone and sodium phenylmercaptide act readily on one another in alcoholic solution at 100°, according to the equation—

$$COMe·CH_2·Cl + SPhNa = NaCl + COMe·CH_2·SPh.$$

The oily product, after mixing with a little benzene, is well shaken with a 3 per cent. solution of permanganate; dilute sulphuric acid being occasionally added, until the solution remains permanently red. After removing the permanganate by alcohol, the solution is extracted with ether, and the semi-crystalline mass recrystallised from alcohol. The compound thus prepared is identical with the phenylsulphonacetone previously prepared by R. and W. Otto. The aqueous solution, after extraction with ether, contains acetic and benzenesulphonic acids, which are products of the further oxidation of phenylsulphonacetone.

Ethyl thiophenylacetoacetate, $SPh·CHAc·COOEt$, obtained from sodium phenylmercaptide and ethyl chloracetoacetate, on oxidation, gives carbonic anhydride, acetic acid, and phenyl bisulphide.

Dichlorhydrin is acted on by sodium phenylmercaptide with formation of a disulphone, $OH·CH(CH_2·SPh)_2$, which is oxidised by potassium permanganate to *symmetrical diphenylsulphonisopropyl alcohol*, $OH·CH(CH_2·SO_2Ph)_2$, a yellow oil insoluble in water, but readily soluble in alcohol and ether. Its *benzoate*, $C_{22}H_{20}OS_2O_6$,

crystallises from alcohol in needles melting at 149—150°. The corresponding ketone, $CO(CH_2·SO_2·Ph)_2$, cannot be obtained by further oxidation, as it then splits up into acetic acid and benzenesulphonic acid. H. G. C.

Replacement of the Sodium in Ethyl Sodiophenylsulphoneacetate by Alkyls. By A. MICHAEL (*Ber.*, **23**, 669—671).—The author has repeated some of the experiments on the synthesis of homologues of ethyl phenylsulphoneacetate which were previously carried out conjointly with Palmer and Comey (Abstr., 1884, 319; 1885, 986), as his results were called into question by Otto and Rössing (Abstr., 1889, 994); he points out that they were unable to obtain ethyl α-phenylsulphonebutyrate, for the simple reason that they used alcohol containing water, and in doing so neglected to follow his directions. F. S. K.

Analogy of Ketonic Acids to Sulphonecarboxylic Acids. By A. RÖSSING (*J. pr. Chem.* [2], **41**, 369—396).—The action of various substances, whose behaviour with ethyl acetoacetate (as a typical ketonic acid) is known, on phenylsulphonacetic acid, ethyl sodiophenylsulphonacetate, and sodium benzenesulphinate was tried. The author summarises the results of his experiments as follows:—(1) β-Sulphonecarboxylic acids ($R·SO_2·CH_2·COOH$) are not split up into other acids by the action of alkalis. (2) The sodium in ethyl sodiophenylsulphonacetate cannot be displaced by acid radicles. Substituted ethereal salts, containing an acetyl- and a sulphone-group, united to the same carbon-atom, cannot be obtained by acting on sodium benzenesulphinate with ethyl mono- or di-chloracetoacetate. (3) The action of iodine on ethyl sodiophenylsulphonacetate in the presence of water in alcoholic solution produces only iodomethylphenylsulphone, and not an ethyl diphenylsulphonesuccinate, nor can a diphenylsulphonesuccinic acid be obtained by the action of sodium benzenesulphinate on mono- or di-bromosuccinic acid. (4) Ethyl chloroxalate decomposes benzene sulphinate, forming carbonic anhydride, phenyl benzenethiosulphonate, and diethyl oxalate; a little ethyl phenylketonesulphonate is formed at the same time. (5) Nitrous acid acts on phenylsulphonacetic acid, forming a *compound*, $(PhSO_2)_2NHO$, which crystallises in leaflets and melts at 98—99° without decomposition; it is not identical with the substance of the same formula obtained by Königs (Abstr., 1878, 573), and contains no hydroxyl-group. (6) Concentrated nitric acid acts on phenyl-sulphonacetic acid, producing *phenylnitrososulphone*, $PhSO_2NO$, which forms white, vitreous crystals melting at 156—157°, and soluble in hot alcohol, benzene, ether, and glacial acetic acid. A. G. B.

Indazole-derivatives. By H. STRASSMANN (*Ber.*, **23**, 714—718).—The author has further examined the reactions of the remarkable compound obtained by Victor Meyer by the action of alkalis on the substance obtained from diazobenzene chloride and ethyl dinitrophenylacetate, to which the provisional constitutional formula

$$\begin{array}{l} NPh\cdot C_6H_4\cdot NO_2 \\ | \quad\;\; | \\ N{=\!=}C\cdot COOK \end{array}$$

has been assigned (Abstr., 1889, 516). The compound in question cannot be reduced by any of the usual means; but the conclusion that it does not contain a nitro-group cannot be drawn, as the compound from which it is obtained, and which undoubtedly contains nitro-groups, is equally stable towards the same reagents.

When the methyl salt of the indazole-compound is heated with hydroxylamine hydrochloride and ethyl alcohol in a sealed tube at 160—180° for eight hours, it is converted into a substance which crystallises in orange rhombohedra or yellow needles, and melts at 158°; this was found, however, to consist, not of an oxime, but simply of the ethyl salt. It may also be prepared by substituting hydrochloric acid for hydroxylamine hydrochloride.

Fuming nitric acid acts on the above methyl salt with formation of a mononitro-compound, $C_{15}H_{10}N_2O_4\cdot NO_2$, which crystallises from acetic acid in white needles melting at 281°. It dissolves with difficulty in ammonia, yields a yellow, flocculent silver salt, and is readily reduced by zinc and hydrochloric acid, forming an amido-compound which, on the addition of alkali, separates in grey flocks, soluble in concentrated acids. The *hydrochloride* forms small, white plates, and gives with platinous chloride and hydrochloric acid a yellow, micro-crystalline precipitate. The nitrate and sulphate are also white and crystalline.

The compound is quite as stable towards fuming sulphuric acid, which converts it into a sulphonic acid, very sparingly soluble in alcohol, and crystallises from that liquid in slender needles which, on heating, carbonise without melting.

As the compound does not split up when subjected to the action of the strongest reagents, the author has endeavoured to throw some light on its constitution by examining the action of amyl nitrite on ethyl dinitrophenylacetate. The compound obtained agreed in composition with none of the substances which might be expected to be formed in the reaction, and requires further investigation.

H. G. C.

Some new Diphenyl-derivatives. By E. TÄUBER (*Ber.*, **23**, 794—798).—*Metadinitrobenzidine*, $NH_2\cdot C_6H_3(NO_2)\cdot C_6H_3(NH_2)\cdot NO_2$ [$(NH_2)_2 : (NO_2)_2 = 4 : 4' : 2 : 6'$], was prepared by dissolving benzidine sulphate in sulphuric acid, and adding potassium nitrate in such quantity as to furnish enough nitric acid for the formation of a dinitro-derivative. The liquid was then poured into water, filtered from a slight precipitate which formed, and saturated with soda or ammonia. The precipitated nitro-compound was collected, dissolved in dilute hydrochloric acid, and, after boiling the solution with animal charcoal, reprecipitated by ammonia, and crystallised repeatedly from alcohol. It melts at 214°, and dissolves in dilute mineral acids, and to some extent in water.

Metadiamidobenzidine, [$(NH_2)_4 = 4 : 4' : 2 : 6'$], was obtained as a hydrochloride by reducing the above dinitro-compound with tin and hydrochloric acid, and removing the tin with hydrogen sulphide. By decomposing the purified hydrochloride with excess of strong aqueous ammonia, the base itself was obtained in small plates melting at 165°. It does not react with orthodiketones, and yields

brown colouring matters with nitrous acid and with diazochlorides; hence it is a *meta*-compound. The author prefers the formula [$(NH_2)_4$ = 4 : 4′ : 2 : 6′] to [4 : 4′ : 2 : 2′] for this substance, because it does not give a diamido-carbazol when heated with hydrochloric acid under pressure, as a compound with the latter constitution would be expected to do.

Metanitrobenzidine, $NO_2 \cdot C_6H_3(NH_2) \cdot C_6H_4 \cdot NH_2$ [$(NH_2)_2 : NO_2$ = 4 : 4′ : 2], was prepared in a similar manner to the dinitro-compound, half the quantity of potassium nitrate being used. On cooling the solution, yellowish metanitrobenzidine hydrogen sulphate,

$$C_{12}H_{11}N_3O_2,H_2SO_4 + \tfrac{1}{2}H_2O,$$

crystallised out, and was purified by recrystallisation from water. When decomposed by ammonia, it yielded the free nitro-base as an oil, which soon solidified to a red, crystalline mass melting at 143°.

Metamidobenzidine [$(NH_2)_2 : NO_2$ = 4 : 4′ : 2].—The hydrochloride of this base was obtained by reducing the nitro-compound with tin and hydrochloric acid. This salt was decomposed by ammonia, and the solution, on being allowed to evaporate spontaneously, deposited the base in long, colourless needles melting at 134°. The brown colouring matters which it yields with nitrous acid and with diazochlorides show that it is a *meta*-compound.

As regards the azo-colouring matters which the above substances yield, it appears that the introduction of one nitro-group in the meta-position with respect to an amido-group weakens the affinity of the dye for the cotton-fibre, whilst the second nitro-group in the meta-position destroys it altogether. C. F. B.

Derivatives of Stilbene and Isostilbene. By V. Redzko (*J. Russ. Chem. Soc.*, 21. 421—430).—In order to find whether the two tolane dichlorides, $C_{14}H_{10}Cl_2$ (α- and β-), are chemically isomeric or only physically, the author has subjected diphenyldichlorethylene, $CPh_2{:}CCl_2$, to the action of hydriodic acid and red phosphorus. On heating a mixture of 2 grams of the dichloride (boiling at 316·5° corr.) with 1 gram of red phosphorus and 30 c.c. of strong hydriodic acid for 20 hours at 170—190°, a mixture of hydrocarbons was obtained, consisting chiefly of diphenylethane and the lower homologues of benzene, the last being products of decomposition of dibenzyl. On changing the conditions of reduction, dibenzyl was obtained. On saturating a solution of tolane in chloroform with chlorine, tolane tetrachloride was obtained.

Phosphorus pentachloride was cooled in a retort, and benzoïn added to it; the more volatile products of the violent reaction were removed by distillation, and the residue extracted with ether. In this way, a mixture of chlorobenzile, $C_{14}H_{10}OCl_2$, with α-tolane dichloride was obtained. Chlorobenzile was found to melt at 61—62°. The author has doubts as to whether β-tolane dichloride has the same symmetrical formula as the α-compound. B. B.

Action of Ammonium Formate on Ketones. By R. Leuckart (*J. pr. Chem.*, [2], 41, 330—340; compare Abstr., 1885, 1215; 1886,

1023; 1887, 376; 1889, 883, 1003).—When ammonium formate ($2\frac{1}{2}$ parts) is heated with benzile (1 part) for five hours at 215—220°, the reaction mixture treated with water and crystallised from alcohol, colourless needles or leaflets of benzilam (m. p. 113°) are obtained (70 per cent. of the benzile used); this formation confirms Japp's formula for benzilam (Abstr., 1884, 313). A small quantity of lophine is obtained at the same time.

When ammonium formate is heated with benzoïn at 230°, ditolane-azotide (m. p. 245°; Japp, Trans., 1886, 828) is obtained, and if phenanthraquinone is substituted for benzoïn, diphenanthrylene-azotide (*ibid.*) is formed.

Ammonium formate simply reduces anthraquinone without forming any additive product.

Acetone was heated with ammonium formate for 4—5 hours in a sealed tube at 210°, and the oil formed mixed with soda and distilled with steam. The colourless distillate was acidified with hydrochloric acid, evaporated, mixed with soda, and shaken with ether; the ether was evaporated, and the residual oil distilled, when the following fractions were obtained:—(1) $C_8H_{15}N$, a colourless, strongly refractive, mobile oil, distilling at 155—156°; it is a strong base, and gives coloured precipitates with solutions of metallic salts; its *hydrochloride* and *platinochloride* were obtained. The yield of this fraction is about 9 per cent. of the acetone. (2) $C_{10}H_{19}N$, a yellow oil which gradually becomes brown; it distils between 195° and 200°, is less soluble in water than the first fraction, and is a strong base. It gives coloured precipitates with solutions of metallic salts. (3) $C_{10}H_{19}N$, a yellowish-brown oil, quite insoluble in water and strongly basic. It distils between 260° and 270°.

All these oils have a peculiar, numbing smell, and are undoubtedly closely allied to the pyridine bases. A. G. B.

Tetrachloro-α-diketohydronaphthalene and its Decomposition-products: Orthotrichloracrylbenzoic Acid and Phthalylchloracetic Acid. By T. ZINCKE and T. COOKSEY (*Annalen*, **255**, 356—392).—It has been shown by Zincke and Frölich (Abstr., 1887, 955) that the dichloro-α-naphthachloroquinone obtained by Claus (Abstr., 1886, 714) is, in reality, a ketochloride-derivative of hydronaphthalene, analogously constituted to the compounds prepared from amido-β-naphthol; it was also shown by Zincke and Kegel (Abstr., 1888, 709) that when Claus' dichloro-α-naphthachloroquinone is treated with alcoholic potash, it is converted into an acid identical with the compound obtained from hexachlorodiketohydronaphthalene; this probably has the constitution $CCl_2{:}CCl{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$. The experiments described below prove that this acid has this constitution; it follows, therefore, that Claus' dichloro-α-naphthachloroquinone is a tetrachloro-α-diketohydronaphthalene of the constitution

$$C_6H_4<\begin{matrix}CO{\cdot}CCl_2\\ |\\ CO{\cdot}CCl_2\end{matrix}.$$

Tetrachloro-α-diketohydronaphthalene, prepared by Claus' method (*loc. cit.*), melts at 117°, and is much more stable than the isomeric compounds.

Orthotrichloracrylbenzoic acid, $CCl_2{:}CCl{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, crystallises in needles or prisms and melts at 126—127°; the metallic salts cannot be obtained owing to their instability. The *methyl* salt, $C_{11}H_7Cl_3O_3$, crystallises from dilute alcohol in well-defined, colourless prisms, melting at 47—48°. The acid is completely decomposed by water at 140—150°, yielding, besides resinous products, a neutral compound, which crystallises in reddish-brown needles, melts at 270°, and is free from chlorine. It is gradually decomposed by cold alkalis, yielding phthalic acid and trichlorethylene, and when treated with aniline in the cold it is converted into phthalanil (m. p. 203°).

Orthopentachloropropionylbenzoic acid, $CCl_3{\cdot}CCl_2{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, is formed when orthotrichloracrylbenzoic acid is heated at 140—150° with manganese dioxide and concentrated hydrochloric acid. It crystallises from glacial acetic acid in prisms, melts at 185—186°, and is moderately easily soluble in alcohol and glacial acetic acid, but almost insoluble in water. It is not acted on by concentrated sulphuric acid at 100°, but when heated alone, it is decomposed into pentachlorethane and phthalic anhydride, which sublimes. It dissolves unchanged in sodium carbonate, but it is immediately decomposed by alkalis yielding phthalic acid and pentachlorethane. The *methyl* salt, $C_{11}H_7Cl_5O_3$, crystallises from dilute alcohol in needles, melts at 78—79°, and is readily soluble in methyl and ethyl alcohol.

Phthalylchloracetic acid, $CO{<}^{O\,-}_{C_6H_4}{>}C{:}CCl{\cdot}COOH$, is produced, together with small quantities of an isomeric acid, chloracetophenonecarboxylic acid, and a compound melting at 104—105°, when orthotrichloracrylbenzoic acid is treated with concentrated sulphuric acid at the ordinary temperature. The solution is poured into water, the precipitate separated by filtration, dissolved in sodium acetate, and the boiling solution acidified with hydrochloric acid, whereupon the phthalylchloracetic acid and its isomeride are precipitated in crystals (and can be separated by crystallising from a mixture of benzene and acetic acid), while the chloracetophenonecarboxylic acid remains in the solution and can be isolated by extracting with ether. Phthalylchloracetic acid separates from a mixture of benzene and acetic acid in slender, silky needles, melts at 233—234° with previous softening, and is readily soluble in alcohol and glacial acetic acid, but only sparingly in acetone and benzene, and almost insoluble in light petroleum. It is gradually decomposed by cold sodium carbonate, and quickly by soda, yielding a yellow, resinous compound, but it dissolves unchanged in cold sodium acetate, and, even on boiling, it is only slowly decomposed. When warmed for a long time with concentrated sulphuric acid, it is converted into a neutral substance, probably tribenzoylenebenzene, which melts at 180°; it is readily oxidised by nitric acid of sp. gr. 1·4, with formation of phthalic acid.

The *anilide* of chloracetophenonecarboxylic acid,

$$NHPh{\cdot}CO{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Cl,$$

is formed, with evolution of carbonic anhydride, when phthalylchloracetic acid is warmed with aniline in alcoholic solution; it separates

from hot alcohol in colourless crystals, melts at 175—176° with decomposition, and is insoluble in water.

Dichloromethylenephthalyl, $CO<\begin{matrix}O-\\C_6H_4\end{matrix}>C:Cl_2$, is easily obtained, together with the tetrachloro-compound (see below), by passing chlorine into glacial acetic acid containing phthalylchloracetic acid in suspension until the acid has completely dissolved. It crystallises from hot alcohol in long, slender needles, melts at 128—129°, and is readily soluble in benzene, glacial acetic acid, and light petroleum. When treated with cold alcoholic potash, it is converted into dichloracetophenonecarboxylic acid, identical with the compound obtained by Zincke and Gerland from dichlorodiketohydrindene: when dichloracetophenonecarboxylic acid is warmed with concentrated sulphuric acid, it is reconverted into dichloromethylenephthalyl.

Tetrachloromethylphthalide (tetrachloromethylenephthalyl),

$$CO<\begin{matrix}O-\\C_6H_4\end{matrix}>CCl\cdot CCl_3,$$

crystallises from dilute alcohol in well-defined, colourless prisms, melts at 93—94°, and is readily soluble in alcohol, glacial acetic acid, and benzene; it is decomposed by alcoholic potash into chloroform and phthalic acid.

The acid $C_{10}H_5ClO_4$, isomeric with phthalylchloracetic acid, is obtained when the mother liquors from the phthalylchloracetic acid (see above) are evaporated to dryness and the residue extracted with hot benzene, in which it is more readily soluble than phthalylchloracetic acid. It crystallises in slender needles. melts at 215—216° with previous softening, and resembles the isomeride in its properties and reactions; when dissolved in cold, concentrated sulphuric acid, it is gradually converted into phthalylchloracetic acid.

Chloracetophenonecarboxylic acid, $COOH\cdot C_6H_4\cdot CO\cdot CH_2Cl$, crystallises from a mixture of ether and light petroleum in thick, colourless needles, melts at 118—119°, and is moderately easily soluble in alcohol, ether, glacial acetic acid. and benzene, but almost insoluble in light petroleum. The *methyl* salt, $C_{10}H_9O_3Cl$, crystallises from dilute alcohol in colourless needles melting at 78—79°. When the acid is treated with chlorine in sodium carbonate solution, it is converted into trichloracetophenonecarboxylic acid (m. p. 142°). the *methyl* salt of which crystallises in colourless needles and melts at 127—128°.

A direct comparison of the acid obtained from hexachloroketohydronaphthalene with the orthotrichloracrylbenzoic acid described above proved the identity of the two compounds; the methyl salts of the two acids were also proved to be identical. F. S. K.

Dichloro-α-naphthaquinone Dichloride. By A. Claus (*J. pr. Chem.*, [2], **41**, 285—291).—In this paper the author replies to a paper of Zincke and Cooksey (preceding abstract), in which they are at variance with him as to the constitution and nomenclature of some naphthaquinone-derivatives. A. G. B.

Azimido-compounds. By T. ZINCKE and C. CAMPBELL (*Annalen*, **255**, 339—356; compare Zincke and Arzberger, Abstr., 1889, 501).—When amido-β-naphthylphenylamine is treated with acetic acid and sodium nitrite, it yields a tertiary azimide, which has quite different properties from the compound of the same composition which is obtained by the oxidation of benzeneazo-β-naphthylamine. The two substances are therefore isomeric, and each belongs to a distinct class of compounds, which may be named *azimides* and *pseudoazimides* respectively. The azimides contain the atomic complex, $\begin{matrix}-N\\-NX\end{matrix}\!\!>\!N$, and are obtained by the action of nitrous acid on orthodiamines or their derivatives; they contain a hydrogen-atom in combination with nitrogen, which can be displaced by metals, acid radicles, and alkyl-groups, and they can be easily converted into tertiary bases and ammonium hydroxides, or their derivatives. The pseudoazimides contain the atomic complex, $\begin{matrix}-N\\ | \\-N\end{matrix}\!\!>\!NX$, and are formed by the oxidation of the orthamidodiazo-compounds and by the decomposition of the diazoimides obtained from the latter; they have not a basic character.

Phenylazimidonaphthalene, $C_{10}H_6<\begin{matrix}N\\NPh\end{matrix}\!\!>\!N$, is obtained when α-amido-β-naphthylphenylamine, or the hydrochloride thereof, is gradually treated with sodium nitrite in cold glacial acetic acid solution. It can also be prepared by treating amidophenylnaphthylamine with excess of amyl nitrite in well-cooled glacial acetic acid solution, and then evaporating to dryness on the water-bath. It crystallises from hot alcohol in colourless needles, and from glacial acetic acid in prisms, melts at 149—150°, and is almost insoluble in water; it is only very sparingly soluble in concentrated hydrochloric acid, and it does not form a platinochloride. The *methiodide*, $C_{17}H_{14}N_3I$, prepared by heating the base with methyl iodide at 100°, crystallises from hot dilute alcohol in colourless needles, melts at 196° with liberation of methyl iodide, and is only sparingly soluble in alcohol, water, and glacial acetic acid; it combines with iodine yielding a *periodide*, which crystallises in reddish-brown needles melting at 127°. The *methochloride*, $C_{17}H_{14}N_3Cl$, prepared by treating the methiodide with silver chloride, is readily soluble in water and alcohol, and crystallises from the last-named solvent in small, colourless needles melting at 183° with decomposition. The *platinochloride*, $(C_{17}H_{14}N_3Cl)_2PtCl_4$, crystallises in small, yellow plates, melts at about 250—251°, and is only sparingly soluble in hot alcohol and glacial acetic acid, and almost insoluble in water. The *compound* $C_{17}H_{14}N_3Cl,ICl$, prepared from the iodide by Zincke and Lawson's method (Abstr., 1887, 730—731), crystallises in broad, yellow needles or plates, and melts at 138—139°. The *hydroxide*, $C_{17}H_{14}N_3{\cdot}OH$, can only be obtained in solution, and it decomposes when its solutions are evaporated; it has a strongly alkaline reaction and an intensely bitter taste, and it decomposes salts of ammonia, iron, and aluminium.

Ethylphenylnaphthaleneazammonium iodide, $C_{16}H_{11}N_3,EtI$, prepared

by heating phenylazimidonaphthalene with ethyl iodide at 100° for 5—6 hours, crystallises in colourless needles, melts at 192° with decomposition, and is moderately easily soluble in hot alcohol, but only sparingly in water. The *periodide* crystallises in brown plates and melts at 113°. The *ethochloride*, $C_{16}H_{11}N_3$,EtCl, obtained by treating the iodide with silver chloride, crystallises in almost colourless needles, melts at 212° with decomposition, and is readily soluble in water and alcohol, but only sparingly in ether. The *platinochloride*, $(C_{18}H_{16}N_3Cl)_2PtCl_4$, crystallises from hot alcohol, in which it is only sparingly soluble, in golden plates, melts at about 264°, and is almost insoluble in water. The *chloriodo*-additive compound forms large, dark-yellow plates melting at 174—176°.

When amidophenylnaphthylamine hydrochloride is treated with amyl nitrite in cold glacial acetic acid solution, the chloro-compound (m. p. 172—173°) previously described by Zincke and Lawson (*loc. cit.*) is obtained.

A compound of the composition $C_{16}H_8N_4O_2$, or $C_{16}H_{10}N_4O_2$, separates in crystals when nitrous acid (prepared from arsenic trioxide and nitric acid) is passed into a well-cooled glacial acetic acid solution of amidophenylnaphthylamine. It crystallises in golden needles, melts at 207—208°, and is readily soluble in hot glacial acetic acid and hot benzene, but only sparingly in hot alcohol; it dissolves in concentrated sulphuric acid yielding a colourless solution, does not give Liebermann's nitroso-reaction, and does not combine with alkyl iodides. When reduced with stannous chloride in warm alcoholic solution, it is converted into a base of the composition $C_{16}H_{12}N_4$; this compound crystallises in colourless needles or plates, melts at 193–194°, and is readily soluble in alcohol, glacial acetic acid, and chloroform, the solutions showing a slight fluorescence. The *hydrochloride*, $C_{16}H_{12}N_4$,HCl, crystallises in colourless needles or plates. The *acetyl*-derivative, $C_{16}H_{11}N_4Ac$, crystallises from hot alcohol, in which it is only sparingly soluble, in colourless needles, melts at 260—261°, and is readily soluble in glacial acetic acid. The *diacetyl*-derivative, $C_{16}H_{10}N_4Ac_2$, is obtained, together with the monacetyl-derivative, by boiling the base for a long time with acetic anhydride and sodium acetate; it crystallises from dilute alcohol in plates, melts at 176—177°, and is readily soluble in glacial acetic acid.

When the hydrochloride of the base (m. p. 193—194°) is suspended in alcohol and treated with a little glacial acetic acid and sodium nitrite, it is converted into a deep-red substance which is almost insoluble in all ordinary solvents, and is reconverted into the base when warmed with a dilute alcoholic solution of stannous chloride.

A compound of the composition $C_{23}H_{16}N_4$ is formed when the base (m. p. 193—194°) is heated with benzaldehyde for a few hours at 130—140°; it crystallises in yellow needles, melts at 137—139°, and is readily soluble in benzene, but only sparingly in light petroleum.

Pseudophenylazimidonaphthalene, $C_{10}H_6<\overset{N}{\underset{N}{|}}>NPh$, prepared by the method previously described by Zincke (Abstr., 1886, 244), melts at 107—108°, and is chiefly characterised by its chemical indifference; molecular weight determinations by Raoult's method in glacial acetic

acid solution gave results in accordance with the molecular formula $C_{16}H_{11}N_3$. F. S. K.

Amidochrysene. By R. Abegg (*Ber.*, **23**, 792—793).—Mononitrochrysene cannot be reduced by the usual agents; hydriodic acid, however, effects the desired result. Pure nitrochrysene, mixed with a little red phosphorus, was gently boiled with hydriodie acid until the original brown colour had changed to grey. The grey powder, evidently the hydriodide of a base, was washed and dried, dissolved in hot alcohol, filtered from unaltered red phosphorus, and treated with concentrated alcoholic potash; the free base, $C_{18}H_{11}\cdot NH_2$, being less soluble in alcohol than its hydriodide, then separated out. It melts at 201—203°, its colour is brown or yellowish-brown, and it dissolves in benzene, nitrobenzene, ether, alcohol, and acetic acid. Its platinochloride, $(C_{18}H_{13}N)_2,H_2PtCl_6$, was obtained as a yellow, crystalline precipitate, which oxidises and turns green when warmed.

C. F. B.

Terpenes from the Oil of Pinus abies. By W. Kouriloff (*J. Russ. Chem. Soc.*, 21, 357—367).—Resin from the fir tree (*Pinus abies*) was distilled with steam and the oil subjected to fractional distillation and purification from oxygen compounds. It contains an inactive terpene and a detro-rotatory isoterpene. The author has carefully determined their physical properties, and compares them with optically isomeric compounds obtained previously by Flavitzky (Abstr., 1887, 968).

	Inactive terpene.	Dextro-terpene.	Dextro-isoterpene.	Lævo-isoterpene.
Boiling point	157°	156°	178·3°	176·7°
Spec. rot. power $[\alpha_D]$..	0	+27·5°	+57·6°	47·5°
Density at 0°	0·8748	0·8764	0·8627	0·8627
Density at 20°	0·8589	0·8600	0·8480	0·8529
Coeff. of dilat.........	0·00093	0·00095	0·00089	0·00087
Mol. refrac. $P\dfrac{A-1}{d}$	71·48	71·24	73·28	73·28

B. B.

Dextrorotatory Terpene from Pinus cembra. By F. Flavitzky (*J. Russ. Chem. Soc.*, 21, 367—375).—A large quantity of the needles of the Siberian cedar (*Pinus cembra*, L.) was subjected to distillation with steam and the oil obtained fractionated and purified. The dextrorotatory terpene hitherto obtained by the author from Russian turpentine had a rotatory power of $[\alpha]_D = +32·45°$ only, whereas the corresponding lævorotatory terpene from French turpentine was found to have a rotatory power of $[\alpha]_D = -43·36°$. Fractionation of the cedar-oil yielded a terpene boiling at 156° (corr.) and having a specific rotatory power $[\alpha]_D = +45·04°$. The density is 0·8746 at 0° and 0·8585 at 20°. Coefficient of dilatation = 0·00094°, molecular refractive power $P\dfrac{A-1}{d} = 71·55$. Analogous values are given for some of its derivatives. The terpene in question is optically isomeric with that from French turpentine, the value of $[\alpha]_D$, found by Flavitzky, being $= -43·36°$, whereas Bouchardat and Lafont

(Abstr., 1886, 475), after allowing the same terpene to remain in contact with glacial acetic acid for six months, found $[\alpha]_D = -44.95°$. The two terpenes are therefore optically isomeric, boiling at 156°, and having a specific rotatory power of $[\alpha] = +45°$ and $-45°$. Both isomerides seem to behave differently towards a solution of 1 per cent. of sulphuric acid in glacial acetic acid, the action on the lævorotatory compound being more energetic. B. B.

Camphoric Acids. By E. JUNGFLEISCH (*Compt. rend.*, **110**, 790—793).—The solubility of ordinary dextrogyrate camphoric acid is practically identical with that of the lævogyrate acid from feverfew camphor, but very different from that of the lævogyrate acid obtained by heating the dextrogyrate acid in presence of water.

When lævogyrate camphoric acid is heated in presence of water, it yields an optically inactive acid, *paracamphoric acid*, which is very similar to mesocamphoric acid, but which can be split up into a lævogyrate acid similar to the original acid and a dextrogyrate acid similar to that obtained from dextrocamphoric acid under like conditions, but with an equal rotatory power of opposite sign. The dextrogyrate and lævogyrate acids obtained in this way, when mixed in equivalent proportions, yield an inactive acid with properties recalling those of the mesocamphoric acids. C. H. B.

Camphorates of the α-Borneols. By A. HALLER (*Compt. rend.*, **110**, 580—583).—The various active and inactive camphoric acids and camphols can yield 72 ethereal salts, 48 of which will be acid salts and 24 normal salt, some of the latter being active and some racemic. The products described in this paper were obtained from dextrocamphoric acid and the α-borneols.

Dextro-α-borneol (2 mols.) and dextrocamphoric anhydride (1 mol.) were heated in sealed tubes at 210—215° for 48 hours. The product was extracted with a mixture of ether and light petroleum and the solution washed with an aqueous solution of sodium carbonate in order to remove the acid ethereal salt. The ether was then distilled off and the residue crystallised from alcohol. The product was insoluble in water and alkalis, but dissolved in ether, benzene, and light petroleum. It had the composition $C_8H_{14}(COO{\cdot}C_{10}H_{17})_2$, but contained at least two substances which could be separated by fractional crystallisation, the extreme melting points being 102° and 128°, and the extreme molecular rotatory powers $[\alpha]_D = +30.83$ and $+52.08$.

The dextrogyrate acid salt is obtained by acidifying the alkaline wash water of the previous operation. It dissolves in alcohol and ether, but is only slightly soluble in light petroleum, from which it crystallises in hard, white nodules melting at 176—178°; molecular rotatory power $[\alpha]_D = +31°$ to $+40°$. When treated with acetic chloride, it yields camphoric anhydride and a chlorine compound which is doubtless borneol chloride. It is only slightly soluble in cold alkalis and alkaline carbonates, but dissolves readily on heating and gelatinises on cooling. If the gelatinous mass is dried and crystallised from alcohol, *sodium borneol camphorate*,

$$COONa{\cdot}C_8H_{14}{\cdot}COO{\cdot}C_{10}H_{17},$$

is obtained in white, crystalline leaflets, which have an alkaline reaction and are decomposed by carbonic acid. With copper salts, its solution gives a blue precipitate which readily splits up into cupric oxide and hydrogen borneol camphorate.

Similar products are obtained in the same way from lævo-α-borneol and dextrocamphoric anhydride. The normal salt crystallises in slender needles melting at 122°. The acid salt dissolves in alcohol, ether, and benzene, but is only slightly soluble in light petroleum; it melts at 164—168° and its molecular rotatory power is $[\alpha]_D = -17°$ to $-25°$. Like its isomeride, it dissolves in alkalis and alkaline carbonates and the solution gelatinises on cooling, has an alkaline reaction, and is decomposed by carbonic anhydride.

If the camphols and camphoric acid are heated at 140°, no normal ethereal salts are obtained.

From these facts it follows (1) that complete etherification of camphoric acid is only obtained at a comparatively high temperature, and when the anhydride is used; (2) in the operation, isomerides are formed owing to alteration of the camphoric acid; (3) in the acid ethereal salts, the acid function resembles that of the phenols rather than that of a true acid. C. H. B.

Phenolsulphonic Acids from Camphor. By P. CAZENEUVE *Compt. rend.*, **110**, 719—722).—The action of concentrated sulphuric acid on camphor yields sulphonic derivatives in small quantities only. If monochlorocamphor is mixed with five times its weight of concentrated sulphuric acid, a reaction takes place at 30° with slow evolution of hydrogen chloride, sulphurous anhydride, and some methyl chloride; at the ordinary temperature, the reaction takes place much more slowly. At least four products are formed and can be separated by fractional crystallisation after neutralisation with barium carbonate. All are sulphonic derivatives and have a phenolic function, which is indicated by the blue or violet coloration produced with ferric chloride, and the formation of acetyl-derivatives.

One has the composition $SO_2{\cdot}C_9H_{12}O(OH)_2$ and contains a phenolic hydroxyl, an alcoholic hydroxyl (secondary), and the ketonic group of the camphor, but no acid hydroxyl. The second has the composition $HSO_3{\cdot}C_{10}H_{18}O{\cdot}OH$ and contains one acid and one phenolic hydroxyl. The third contains three sulphonic acid groups and at least one phenolic hydroxyl, and has the formula $(HSO_3)_3{\cdot}C_{10}H_{18}O_5{\cdot}OH$, but the exact number of phenolic or alcoholic hydroxyls and the existence or non-existence of a ketonic group have still to be ascertained. The fourth compound contains one or several hydroxyl-groups and one or several phenolic groups, but is very difficult to purify, and its composition has not yet been definitely ascertained.

The author regards these results as conclusive proof of the presence of a benzene nucleus in the terebene-group. The formation of phenols by the combination of the hydroxyl of sulphuric acid with a benzenoïd nucleus has not been observed before. C. H. B.

Constituents of Quassia amara, L., and Picraena excelsa, Linds. By F. MASSUTE (*Arch. Pharm.* [3], 28, 147—171).—The

coarsely-powdered drug *Quassia amara* was digested three times with 50 to 60 per cent. alcohol, the liquids mixed and treated with a little freshly-burnt magnesia, a little acetic acid added if necessary to produce a slight acid reaction, and the solution filtered, after which the alcohol was expelled at the lowest possible temperature. The aqueous solution thus obtained was warmed gently in an open dish, and the water was replenished from time to time, so as to get rid of all alcohol. On cooling, the separated resin was removed, and the liquid repeatedly shaken up with chloroform. From the separated chloroform solution, the chloroform was distilled off, and the residue treated with a mixture of absolute alcohol and ether; this was evaporated and the residue was dissolved in absolute ether, which, on slow evaporation, gave crystals of quassiin, which further treatment with ether and alcohol rendered quite pure. This process insures the isolation of the bitter principle actually existing in the plants, and avoids the formation of decomposition-products. Repeated recrystallisation of the product led to the separation of four compounds differing in their solubilities and melting points. The melting points were 210° to 211°, 215° to 217°, 221° to 226°, and 239° to 242°. The first and last compounds could not be further examined owing to the lack of material; but the former agrees with the quassiin obtained by first boiling the wood with water as in Christensen's extraction method, and in crystalline form and melting point is the same as that observed by Wiggers, and by Oliveri and Denaro. Quassiin, melting point 215° to 217°, on analysis gave $C_{35}H_{46}O_{10}$. and that with melting point 221° to 226° gave $C_{37}H_{50}O_{10}$. The bitter principle picrasmin, obtained as above from *Picraena excelsa*, melted at 206° to 208° and was a mixture of two varieties melting at 204° and at 209—212° respectively. Some commercial crystalline material was purified, and the two varieties were readily isolated; that melting at 204° was found to have the formula $C_{35}H_{46}O_{10}$ whilst the other gave $C_{36}H_{48}O_{10}$. It is probable that quassiin and picrasmin are not identical but form two series of homologous compounds. To elucidate this point, some of the decomposition-products of picrasmin were studied. Hydrochloric acid in a closed tube with picrasmin produced *picrasmic acid;* the barium salt of this acid was analysed and showed the acid to be bibasic; its formation may be thus represented $C_{31}H_{40}O_6(COOMe)_2 + 2HCl = C_{31}H_{40}O_6(COOH)_2 + 2MeCl$. Zeisel's reaction, in which picrasmin is treated with fuming hydriodic acid in a current of carbonic anhydride, shows that three methoxyl-groups are present, but only two of these were attached to carboxyl, as shown by treatment with hydrochloric acid. Quassiinic acid, $C_{30}H_{38}O_{10}$, obtained by Oliveri and Denaro, and picrasmic acid, $C_{33}H_{42}O_{10} + 5H_2O$, obtained by the author, strengthen the view of the non-identity of quassiin and picrasmin. J. T.

Action of Acids on Litmus. By J. E. MARSH (*Chem. News*, **61**, 2). —Attention is drawn to the fact that concentrated and Nordhausen sulphuric acids, glacial acetic acid, dry propionic, butyric, and valeric acids do not redden dry litmus paper; it is therefore inferred that the conversion of blue into red litmus requires the presence of water.

The reddening of litmus by strong nitric acid is attributed to the decomposition of the organic matter with the liberation of water.

D. A. L.

Preparation and Properties of certain Pyrrolidone-derivatives. By O. KÜHLING (*Ber.*, **23**, 708—713).—In addition to the compounds described in his previous paper (Abstr., 1889, 1211), the author has now succeeded in obtaining certain new pyrrolidone-derivatives by the action of ethylamine on the cyanhydrin of ethyl levulinate, and has also prepared the amide of 2-methylpyrrolidone-2-carboxylic acid. The latter is formed by adding 2-methylpyrrilidone-2-carbonitrile to well-cooled sulphuric acid, allowing the mixture to remain for a few hours, then pouring it into water, neutralising with sodium carbonate, and evaporating to dryness. The residue is extracted with alcohol, and the inorganic matter removed by repeated evaporation to dryness and extraction with alcohol. The amide, $\begin{matrix} CH_2{\cdot}CH_2 \\ | \\ CO-NH \end{matrix}\!\!>\!CMe{\cdot}CONH_2$, forms white, crystalline crusts, consisting of stellate aggregates of slender needles which melt at 161°, and are very soluble in water, less so in alcohol, and insoluble in ether. The corresponding acid and its salts could not be obtained in the crystalline form.

The action of ethylamine on the cyanhydrin of ethyl levulinate was allowed to take place under the same conditions as that of aniline (*loc. cit.*), and the resulting nitrile, which could only be obtained as an oil, added to cooled concentrated sulphuric acid. The 1-*ethyl-2-methylpyrrolidone-2-carboxylamide*, $\begin{matrix} CH_2{\cdot}CH_2 \\ | \\ CO-NEt \end{matrix}\!\!>\!CMe{\cdot}CONH_2$, thus formed was separated and purified in the manner described above. It crystallises from alcohol in needles or prisms which melt at 183°, and dissolve readily in water and alcohol, but not in ether.

1-*Ethyl-2-methylpyrrolidone-2-carboxylic acid*,

$$\begin{matrix} CH_2{\cdot}CH_2 \\ | \\ CO-NEt \end{matrix}\!\!>\!CMe{\cdot}COOH,$$

is best prepared by boiling the pure amide with a slight excess of caustic potash solution, and after concentrating the solution, adding the requisite quantity of acid. The liquid is again evaporated, and the residue extracted with alcohol, the evaporation and extraction repeated several times, and the acid finally crystallised from benzene. It forms stellate aggregates of vitreous needles, and sometimes, on slow evaporation, separates in long, dendritic crystals. It melts at 123°, and is very readily soluble in water and alcohol, less so in hot benzene, and still less in ether. The *salts* of the acid could not be obtained crystalline.

1-*Ethyl-2-methylpyrrolidone-2-carbothioxylamide*,

$$\begin{matrix} CH_2{\cdot}CH_2 \\ | \\ CO-NEt \end{matrix}\!\!>\!CMe{\cdot}CSNH_2,$$

is obtained by passing hydrogen sulphide through an alcoholic solution of the above nitrile, to which a little ammonia has been

added. It crystallises from alcohol in short, white, lustrous prisms which melt with decomposition at 176°.

The *amidoxime* of this series is obtained by boiling the foregoing thiamide with equivalent quantities of hydroxylamine hydrochloride and sodium carbonate; it crystallises from water in slender needles or small plates, which are readily soluble in water and alcohol.

From the results shown in this and the previous paper, it appears that the stability and power of crystallisation of the nitriles, amides, and acids are greatest in the compounds derived from aniline, and least in those derived from ammonia, those derived from ethylamine occupying an intermediate position. H. G. C.

Pyridines: their Relation to Quinoline, Isoquinoline, and the Alkaloids. By A. EDINGER (*J. pr. Chem.* [2], **41**, 341—359).—The author has sought to arrive at the constitution of the bases obtained by the action of moist silver oxide and of alkaline hydroxides on alkylpyridyl halogen-compounds, by comparing their more stable and more easily purified double compounds.

When benzylpyridyl platinochloride, $(C_5NH_4 \cdot C_7H_7)_2,H_2PtCl_6$, is precipitated in aqueous solution, it is anhydrous and melts at 221° (uncorr.); but when it is precipitated in alcoholic solution, it melts at 199° (uncorr.), and contains $\frac{1}{2}$ mol. alcohol of crystallisation. Both forms are slender needles, and are insoluble in water and alcohol.

When benzylpyridyl chloride is treated with silver oxide and water under ether, the aqueous solution of the base obtained gives an anhydrous platinochloride melting at 220° (uncorr.), and identical with the above. A dark-red, crystalline carbonate was obtained when the aqueous solution of the base was saturated with carbonic anhydride and evaporated. The hydrochloric acid solution of the base is not precipitated by ammonia.

When the saponification is performed with potassium or sodium hydroxide, the platinochloride is most easily obtained from an alcoholic solution; it then melts at 199° and contains $\frac{1}{2}$ mol. alcohol of crystallisation. The platinochloride obtained from aqueous solution darkens without melting at 290°, and contains 12 mols. H_2O. The base gives no carbonate, and is precipitated by ammonia.

The paper concludes with some remarks on the constitution of pyridine, quinoline, and isoquinoline. A. G. B.

Pyridine-derivatives from Propaldehyde-ammonia, and Propaldehyde. By E. DÜRKOPF and H. GÖTTSCH (*Ber.*, **23**, 685—693).—When a mixture of propaldehyde-ammonia and propaldehyde, in the proportion of 1 mol. of the former to 2 mols. of the latter, is heated in a sealed tube for six hours at 205—210°, a reddish-brown oil is formed, consisting chiefly of bases belonging to the pyridine-group. The reaction which here takes place is of a character similar to that occurring between aldehyde-ammonia and paraldehyde under similar conditions (Abstr., 1887, 1314). The secondary bases were separated from the crude oil by treatment with potassium nitrite in hydrochloric acid solution, and the residual mixture of tertiary bases separated by

20 fractionations into two chief fractions boiling at 197—199° and 219—221° respectively.

The first-named fraction, after being purified by conversion into the mercury double salt, yielded a colourless base, boiling at 198—199° (corr.) under 763·5 mm. pressure, and agreeing in almost all its properties with the parvoline obtained by Waage and Hoppe (Abstr., 1884, 172; 1889, 120); it has, however, a feeble, not unpleasant odour, the coneïne-like smell observed by Waage and Hoppe being probably due to an admixture of secondary bases. The crystallographic examination of the *platinochloride*, $C_9H_{13}N,H_2PtCl_6$, agrees well with that of Waage's parvoline platinochloride; it forms fairly large, monoclinic crystals melting at 189°, readily soluble in hot, sparingly in cold water. The two bases must, therefore, be identical. The *aurochloride*, $C_9H_{13}N.HAuCl_4$, and the *mercury double salt*, $C_9H_{13}N,HCl,3HgCl_2$, described by Hoppe as oils, were both obtained crystalline, and melt at 81—82° and 117—119° respectively.

On very moderate oxidation with potassium permanganate, the base yielded an acid which could not be obtained free from potash, but which, from the analysis of its platinochloride, must be a dimethyl- or ethyl-pyridinemonocarboxylic acid. It melts at 150—151°, and its *platinochloride*, which crystallises with 1 mol. EtOH, separates from alcohol in slender needles which are very soluble in water and gradually decompose at 260°.

By the further action of potassium permanganate, parvoline yields a methylpyridinedicarboxylic acid, which is also formed in small quantity in the preparation of the foregoing acid; hence the latter must be a dimethylpyridinecarboxylic acid, and the parvoline itself a dimethylethylpyridine. As the methylpyridinedicarboxylic acid here obtained is identical with that formed by the oxidation of Dürkopf and Schlaugk's parvoline, it is probable that the side-chains occupy the 2 : 3 : 5 positions, which is confirmed by the fact that on complete oxidation of Waage's parvoline with warm potassium permanganate, carbodinicotinic acid, $C_5NH_2(COOH)_3$, is obtained. It forms hard, spherical, crystalline aggregates, melts at 318°, and forms an acid silver salt which crystallises in rosette-like aggregates of small plates.

These facts show that Waage's parvoline agrees in almost all its properties and reactions with the parvoline previously obtained by the authors from propaldehyde-ammonia and paraldehyde. The latter differs from Waage's base only in its boiling point (188°) and in the crystallographic properties of its *platinochloride*. The lower boiling point may have been caused by some impuricy, or may be different according to the different methods of preparation (compare β-picoline). A fresh preparation of the *platinochloride* gave crystals agreeing in properties with those of Waage; but as the crystals previously measnred were no longer in existence, the possibility of dimorphism is not excluded. A further proof of their identity is found in the fact that Dürkopf and Schlaugk's base gives on reduction a parpevoline identical with that described below.

The secondary base, isolated from the crude oil by means of its nitroso-compound, is a colourless, mobile liquid, which boils at 176—177°,

and has a penetrating odour resembling that of decaying hay. It has a sp. gr. of 0·8474 at 20° (water at 4° = 1), and a molecular volume of 143·3. The analysis shows its formula to be $C_9H_{19}N$, which has been confirmed by a determination of its vapour-density. It is identical with the hydro-base obtained by the reduction of both Waage's and Dürkopf and Schlangk's base, and is, therefore, a parpevoline. It forms a hygroscopic *hydrochloride* and *hydriodide*, whilst platinum chloride, gold chloride, and picric acid give oily precipitates. The *cadmioiodide*, $(C_9H_{19}N,HI)_2CdI_2$, crystallises in white, sparingly soluble needles which melt at 120—130°.

The fraction of the original oil boiling at 219—221° was purified by conversion into the platinochloride, and forms a colourless oil which boils at 216—217° (uncorr.), is unaltered in air or light, and has likewise the composition of a parvoline, $C_9H_{13}N$. Its *platinochloride*, $C_9H_{13}N,H_2PtCl_6$, forms yellow, sparingly soluble needles or prisms, which do not melt at 270°; the *aurochloride*, $C_9H_{13}N,HAuCl_4$, crystallises in slender, lemon-yellow needles melting at 138—140°, and the *mercurochloride* separates from water containing hydrochloric acid in long, lustrous spangles, or well-developed crystals, probably belonging to the monoclinic system. The base, on oxidation, yields acids which are being further examined. H. G. C.

Action of Quinoline on Copper Sulphate. By E. Borsbach (*Ber.*, **23**, 924—925).—The basic salt which is precipitated when a concentrated solution of copper sulphate is shaken with quinoline has the composition $2CuSO_4,3Cu(OH)_2 + 4H_2O$, and not $3C_9H_7N,2CuSO_4 + H_2O$, as stated by Lachowicz (*Monatsh.*, **10**, 884). F. S. K.

Action of Phenylhydrazine on Ethyl Thiacetoacetate. By K. Buchka and C. Sprague (*Ber.*, **23**, 847—855; compare this vol., p. 28).—*Thiophenylmethylpyrazolone*, $\left[\begin{matrix}NPh{\cdot}CO \\ | \\ N:CMe\end{matrix}\!\!>\!CH\right]_2S$, is formed when a glacial acetic acid solution of phenylhydrazine (2 mols.) is gradually added to a cold glacial acetic acid solution of ethyl thioacetoacetate (1 mol.); on keeping, the base separates in yellow crystals, and can be purified by converting it into the crystalline hydrochloride. It can also be prepared by gradually adding a chloroform solution of sulphur dichloride to a well-cooled chloroform solution of phenylmethylpyrazolone, and decomposing the salt which is produced. It crystallises from alcohol, benzene, or acetic acid in small, colourless plates: the crystals in all cases retain some of the solvent, which is slowly given off on exposure to air, but quickly at 100°. It decomposes at about 183°, but without melting; it is soluble in alkalis and in baryta-water, and it forms stable salts with strong acids. The *hydrochloride*, $C_{20}H_{18}N_4SO_2,HCl$, separates from alcohol in colourless crystals containing 1 mol. of alcohol. When the base is warmed with excess of phenylhydrazine, it is converted into phenylmethylpyrazoloneketophenylhydrazone, small quantities of di-phenylmethylpyrazolone being also formed. It is, doubtless, identical with the compound prepared by Michaelis and Philips (this vol., p. 582) by treating phenylhydrazine with ethyl thioacetoacetate in cold glacial

acetic acid, and to which they assigned provisionally the composition $C_{20}H_{22}O_4N_4S$. F. S. K.

Brominated Derivatives of 1-Phenylpyrazole. By L. BALBIANO (*Gazzetta*, **19**, 128—134).—1-Phenylpyrazole is obtained by heating a solution of epichlorhydrin (50 grams) in benzene (150 grams) with phenylhydrazine (120 grams) for eight to nine hours, and distilling off the benzene. The residue is mixed with sulphuric acid (400 grams containing 10 per cent. acid), distilled in a current of steam, and the ethereal extract of the distillate freed from ether and redistilled. The yield is 58 per cent.

1-*Phenylbromopyrazole*, $C_3N_2H_2BrPh$, is prepared by adding a solution of bromine (11·1 parts) in concentrated acetic acid (20 parts) to a very cold solution of 1-phenylpyrazole (10 parts) in acetic acid (10 parts), allowing the mixture to remain for an hour, and precipitating with water. The yield is theoretical. It crystallises from boiling 95 per cent. alcohol in large, white, lustrous needles, melts at 80·5—81° (corr.), and boils at 293—296° with partial decomposition. It dissolves in alcohol, ether, benzene, and chloroform, especially when warmed, but it is insoluble in water. It has feeble basic properties, and dissolves in concentrated sulphuric, hydrochloric, and acetic acids, but it is reprecipitated unaltered on diluting the solution. Hydroxyl cannot be substituted for the bromine in this compound by the action of potassium hydroxide, nor can a hydrocarbon radicle be introduced by Fittig's or by Friedel and Craft's method. It has also been ascertained that only one of the three possible isomeric 1-phenylbromopyrazoles is formed by the above process, and that the substitution of bromine for the hydrogen-atom takes place without any intermediate additive product being formed.

The *platinochloride*, $(C_3N_2H_2BrPh)_2,H_2PtCl_6,1\frac{1}{2}H_2O$, forms minute-pointed, orange-coloured prisms which decompose at 160—170° without melting. It is decomposed by water and slowly on exposure to the air.

1-*Phenyldibromopyrazole*, $C_3N_2HBr_2Ph$, is obtained by adding bromine (14·5 grams) dissolved in acetic acid (15 grams) to a solution of 1-phenylbromopyrazole (20 grams) in acetic acid (170—180 grams), and precipitating with water after the lapse of a few hours. The yield is about 93 per cent. The dibromo-derivative crystallises from alcohol in large, soft, white, lustrous, flattened needles, melts at 83·5—84° (corr.), dissolves in hot alcohol and benzene, sparingly in cold alcohol and is insoluble in water. It is more feebly basic than the monobrominated derivative, dissolving in concentrated sulphuric acid, but only sparingly in fuming hydrochloric acid and in glacial acetic acid. On mixing hydrochloric solutions of 1-phenyldibromopyrazole and of platinic chloride, a platinochloride is obtained in minute, bright-yellow needles which decompose on drying in the air.

1-*Phenyltribromopyrazole*, $C_3N_2Br_3Ph$, is prepared by boiling a solution of either the mono- or the dibromo-derivative in acetic acid or chloroform with the theoretical amount of bromine. It crystallises from alcohol in groups of slender, silky, colourless needles, melts at

106·5—107 (corr.), and is moderately soluble in alcohol, ether, and chloroform when heated, but only very sparingly in the cold. It is insoluble in water, dissolves with difficulty in concentrated sulphuric acid, and is almost insoluble in fuming hydrochloric acid.

S. B. A. A.

Action of Acid Chlorides on 1-Phenylpyrazole. By L. BALBIANO (*Gazzetta*, **19**, 134—141).—1-*Phenylacetylpyrazole*, $C_3N_2H_2AcPh$, is obtained by heating 1-phenylpyrazole (10 grams) and acetic chloride (40 grams) at 140—150° for eight hours in a sealed tube. The product is freed from acetic chloride by distillation, nearly neutralised with a hot solution of sodium carbonate, and extracted with water; on cooling, phenylacetylpyrazole separates out. It crystallises from dilute alcohol in small, opaque, white needles, which melt at 121·5—122·5° (corr.) to a faintly-yellowish liquid. It is soluble in methyl alcohol and in ethyl alcohol, especially on warming, only moderately in hot water, and very sparingly in cold. It is not sensibly altered by boiling for an hour with a 25 per cent. solution of potassium hydroxide. The ketonic nature of this compound is evident from the formation of an oxime and a hydrazone.

1-*Phenylacetylpyrazoleoxime*, $C_3N_2H_2Ph{\cdot}CMe{:}NOH$, is obtained by boiling a solution of phenylacetylpyrazole (1 mol.) and of hydroxylamine hydrochloride (1 mol.) in methyl alcohol with an aqueous solution of sodium carbonate (1 mol.) for four or five hours. The product is filtered, evaporated on the water bath, and the residue extracted with boiling alcohol. On cooling, the oxime crystallises out in spherical groups, consisting of minute, white needles; it softens at 105°, and melts at 129—131° to a yellowish liquid; on resolidifying, it forms a glassy, transparent mass. It is soluble in alcohol, especially on warming, very moderately so in hot water, and very sparingly in cold water. It dissolves in concentrated hydrochloric acid, and on boiling the solution, it is split up into phenylacetylpyrazole and hydroxylamine hydrochloride.

1-*Phenylacetylpyrazolephenylhydrazone*, $C_3N_2H_2Ph{\cdot}CMe{:}N_2HPh$, is prepared by mixing a hot alcoholic solution of phenylacetylpyrazole (1 mol.) with a hot, aqueous solution of phenylhydrazine hydrochloride (1 mol.) and sodium acetate (1 mol.). It crystallises from boiling alcohol acidified with acetic acid in small, slender, yellowish needles which dissolve in hot alcohol, and melt with decomposition at 142—144°. On boiling with hydrochloric acid, it splits up into phenylacetylpyrazole and phenylhydrazine hydrochloride.

1-*Phenylbenzoylpyrazole*, $C_3N_2H_2BzPh$, is prepared by heating phenylpyrazole (10 grams) and benzoic chloride (40 grams) in a sealed tube at 240—250° for 10 hours. The product is made slightly alkaline with aqueous sodium carbonate, filtered hot, and extracted with hot alcohol. On cooling, phenylbenzoylpyrazole crystallises out in slender, lustrous, white needles which melt at 122—123 (corr.). It is soluble in hot alcohol, very moderately so in hot water, and very sparingly in cold water. The ketonic nature of this compound is likewise shown by the formation of an oxime and a hydrazone.

1-*Phenylbenzoylpyrazolephenylhydrazone*, $C_3N_2H_2Ph{\cdot}CPh{:}N_2HPh$, is prepared like the corresponding acetyl-derivative; it crystallises

from alcohol in small, yellowish-white needles, melts with decomposition at 138—140°, and dissolves in hot alcohol, but not in water. On boiling with hydrochloric acid, it is split up into 1-phenylbenzoylpyrazole and phenylhydrazine.

1-*Phenylbenzoylpyrazoleoxime*, $C_3N_2H_2Ph{\cdot}CPh{:}NOH$, prepared like the corresponding acetyl-derivative, crystallises from alcohol in lustrous, nacreous laminæ, softens at 148°, and melts at 152—154°. It dissolves in alcohol, but is almost insoluble in cold water. Prolonged boiling with hydrochloric acid splits it up into 1-phenylbenzoylpyrazole and hydroxylamine.

The experiments described confirm the analogy between pyrroline and pyrazole-derivatives. S. B. A. A.

Two Pyrazolebenzoic Acids. By L. Balbiano (*Gazzetta*, **19**, 119—128; compare Abstr., 1887, 1054; 1889, 1215). *Parapyrazolebenzoic acid*, $C_3N_2H_3{\cdot}C_6H_4{\cdot}COOH$ [$C_3N_2H_3$: COOH = 4 : 1], is obtained when paratolylpyrazole (6 grams) is dissolved in a dilute solution of potassium hydroxide, and gradually added to a solution of potassium permanganate (12 grams) in water (200 c.c.). As soon as the liquid is decolorised, the unaltered pyrazole is distilled off in a current of steam, the residue filtered, precipitated with dilute sulphuric acid, washed, and thoroughly dried. The acid crystallises from absolute alcohol in small, faintly-yellowish needles, and melts at 264—265° (corr.) to a reddish-yellow liquid. It is almost insoluble in cold water, dissolves very sparingly in warm water or cold alcohol, and only moderately in warm alcohol, ether, or acetic acid It dissolves in concentrated sulphuric acid and in fuming hydrochloric acid, being precipitated again unaltered on diluting the solution. The hydrochloric solution gives no precipitate with a concentrated acid solution of platinic chloride. Its boiling alcoholic solution, after treatment with sodium and with sulphuric acid, gives no coloration either with potassium dichromate or with ferric chloride.

The *ethyl salt* is obtained by adding twice its volume of absolute alcohol to the hydrochloric solution of the acid, saturating with dry hydrogen chloride, and after some time expelling the excess of alcohol and hydrochloric acid, saturating the residue with sodium carbonate, and extracting with ether. The ethyl salt crystallises from hot alcohol in yellowish-white needles, or in shining, unctuous plates; it melts at 61—62° (corr.), and dissolves in alcohol and in ether, especially on warming. It does not take up hydrogen when its alcoholic solution is treated with sodium, &c., but the acid (m. p. = 264°) is reproduced.

The *sodium salt*, $C_{10}H_7N_2O_2Na$, crystallises from dilute alcohol in small, white, anhydrous needles, grouped together in spherical masses, which are very soluble in cold water, but less so in dilute alcohol.

The *barium salt* forms small, anhydrous, white, unctuous laminæ having a silky lustre, it is moderately soluble in hot water, less so in cold. With calcium chloride and zinc sulphate, the sodium salt also gives precipitates soluble in hot water, whilst the precipitates with lead acetate, mercuric chloride, silver nitrate, and copper sulphate are insoluble.

Orthopyrazolebenzoic acid, $C_3H_3N_2 \cdot C_6H_4 \cdot COOH$ [$C_3N_2H_3 : COOH = 2 : 1$], is obtained by the oxidation of orthotolylpyrazole in the way already described for the para-compound. It crystallises from boiling 50 per cent. alcohol in large, bright-yellow, prismatic needles, which have a vitreous lustre and melt at 138·5—139° (corr.) to a bright yellow liquid. It is soluble in warm water, alcohol, and ether, and sparingly in cold water, it dissolves in fuming hydrochloric acid, but no precipitate is obtained on diluting the solution, or on adding platinic chloride; it likewise dissolves in concentrated sulphuric acid. It does not take up hydrogen when its boiling alcoholic solution is treated with sodium, &c.

The *ethyl salt* is obtained by digesting a solution of the acid in 95 per cent. alcohol with one-third its volume of concentrated sulphuric acid for three to four hours at 50—60°. After remaining for some time, the solution is diluted with water, saturated with sodium carbonate, and the oil which separates out is extracted with ether. When pure, it is a yellow oily liquid, which boils at 308—310° (in vapour) and remains liquid at −10°. It is soluble in alcohol and ether, but not in water; it does not take up hydrogen on treating its alcoholic solution with sodium, but the free acid is reproduced. The *barium salt* forms crystalline incrustations, consisting of superposed flattened prisms, the crystals are hard, anhydrous, and readily soluble in water. The *sodium salt* is very soluble in water, and the solution gives with silver nitrate and with mercuric chloride a deposit of small, white crystals soluble in hot water, but no precipitate with either calcium chloride, copper sulphate, lead acetate, or zinc sulphate.

From the above experiments, it appears that bisubstituted phenols in which one hydrogen-atom is displaced by a carbazotic nucleus behave similarly to other bisubstituted phenols, the para-compounds having higher melting points than the ortho-compound, &c. The author considers that the inability of the pyrazole in these compounds to form pyrazoline by hydrogenation indicates that this property is dependent upon the position and character of the other substituting radicle.

S. B. A. A.

Oxidation of Orthophenylenediamine. By O. FISCHER and E. HEPP (*Ber.*, **23**, 841—847; compare Abstr., 1889, 499).—Diamidophenazine hydrochloride has the composition $C_{12}H_{10}N_4,HCl + 3H_2O$, and not $C_{24}H_{18}N_6O,2HCl + 5H_2O$, as stated by Wiesinger (Abstr., 1884, 1322). The *sulphate*, $(C_{12}H_{10}N_4)_2,H_2SO_4 + 3H_2O$, forms crystals very like those of anhydrous chromic acid; Wiesinger's formula for this compound is also incorrect.

Diformyldiamidophenazine, $C_{14}H_{10}N_4O_2$, prepared by boiling the diamido-compound for several hours with sodium formate and concentrated formic acid, is a reddish-yellow compound, very sparingly soluble in water, alcohol, benzene, ether, &c.

A quinoxaline of the composition $C_{26}H_{16}N_4$ is formed when an alcoholic solution of diamidophenazine is boiled with benzile for $1\frac{1}{2}$ hours, glacial acetic acid then added, and the mixture boiled again for an hour. It crystallises from toluene in shining, reddish-brown plates, decomposes when heated, and dissolves in concentrated

sulphuric acid yielding a deep blue solution, the colour of which disappears on adding water. The formation of this quinoxaline proves that diamidophenazine is an orthodiamido-compound, so that it has the constitution $C_6H_4{<}\begin{matrix}N\\ |\\ N\end{matrix}{>}C_6H_2(NH_2)_2\ [(NH_2)_2 = 2 : 3]$.

Dihydroxyphenazine, $C_{12}H_8N_2O_2$, is formed, with liberation of ammonia, when diamidophenazine is heated at 200° with concentrated hydrochloric acid; the reddish-brown, crystalline salt obtained in this way is decomposed with dilute soda, and the base purified by converting it into the sulphate. It crystallises from dilute alcohol in reddish-yellow needles with ½ mol. H_2O, and loses its water at 100°, but only very slowly. The *sulphate*, $(C_{12}H_8N_2O_2)_2,H_2SO_4 + 2H_2O$, crystallises well from dilute sulphuric acid. The *diacetyl*-derivative, $C_{16}H_{12}N_2O_4$, crystallises from hot benzene in yellowish plates, melts at 230°, and is only a feeble base.

The compound obtained by Hübner and Frerichs (this Journal, 1876, ii, 309; and Abstr., 1878, 143) by treating orthophenylenediamine with cyanogen iodide, is diamidophenazine, and has not, therefore, the composition $C_{13}H_{12}N_4$.

The *hydrochloride*, $C_{16}H_{11}N_3,HCl$, separates, on cooling, in red crystals, when orthophenylenediamine (1 mol.) is heated with benzeneazo-α-naphthylamine hydrochloride (1 mol.) and alcohol (10 parts) at 160°; it crystallises from hot alcoholic hydrochloric acid in slender, garnet-red needles, and dissolves in warm water with an orange-red coloration, but is gradually decomposed when the solution is boiled. The free *base*, $C_{16}H_{11}N_3$, crystallises from boiling alcohol in shining plates or slender, yellow needles, melts at 264°, and is insoluble in water and alkalis, and only sparingly soluble in benzene, ether, and cold alcohol, the solutions showing a yellowish-green fluorescence; it dissolves in concentrated hydrochloric acid and in sulphuric acid with a green coloration. The *platinochloride*, $(C_{16}H_{11}N_3)_2,H_2PtCl_6$, crystallises in slender, red needles, and is only sparingly soluble. The *aurochloride*, $C_{16}H_{11}N_3.HAuCl_4$, crystallises in yellowish-red plates, and is rather sparingly soluble in water and alcohol. The *acetyl*-derivative, $C_{18}H_{13}N_3O$, separates from glacial acetic acid as a light yellow, crystalline powder, and is very sparingly soluble in acetic anhydride.

When the compound $C_{16}H_{11}N_3$ described above is heated for some hours at 180—200° with concentrated hydrochloric acid, it is decomposed into ammonia, and the hydrochloride of a base of the composition $C_{16}H_{10}N_2O$. This *base* crystallises from alcohol in reddish needles; it has also the properties of a phenol, and dissolves in hot dilute soda, yielding a reddish-yellow solution from which it is precipitated on the addition of dilute acetic acid. When distilled with zinc-dust, it yields naphthaphenazine (m. p. 142°), so that the compound obtained from orthophenylenediamine and benzeneazo-α-naphthylamine is *α-amido-α-naphthaphenazine*, $NH_2{\cdot}C{\ll}\begin{matrix}CH-C{\cdot}N\\ \quad\ \| \quad |\\ C_6H_4{\cdot}C{\cdot}N\end{matrix}{>}C_6H_4$, analogously constituted to the eurhodine, $C_{17}H_{13}N_3$, obtained by Witt from orthamidoazotoluene and α-naphthylamine.

F. S. K.

Nitro- and Chloro-derivative of β-Methyl-δ-hydroxyquinazoline. By H. DEHOFF (*J. pr. Chem.* [2], **41**, 368).—*Nitro-β-methyl-δ-hydroxyquinazoline*, $NO_2\cdot C_6H_3<\substack{C(OH)\\N:CMe}>N$, is obtained by adding anhydracetylorthamidobenzamide to red fuming nitric acid; it crystallises from alcohol as a yellow powder; it is an acid. Its *methyl-derivative* forms short, almost colourless needles melting at 165°.

When anhydracetylorthamidobenzamide is heated with phosphorus pentachloride at 170°, a substance $C_9H_4Cl_4N_2$ is obtained; this crystallises from alcohol in slender, white, felted needles, and melts at 124—125°. With potash, it yields a compound, $C_9H_5Cl_3N_2O$, which crystallises in yellow prisms melting at 206—207°. The *ethyl-compound* of this last substance crystallises in lustrous, white needles melting at 75°. A. G. B.

γ-Coniceïne, Conyrine, and Inactive Coniïne. By E. LELLMANN and W. O. MÜLLER (*Ber.*, **23**, 680—684).—The coniceïne previously described by Lellmann (Abstr., 1889, 901) has proved to be identical with the γ-coniceïne obtained by Hofmann from coniïne, bromine, and soda (Abstr., 1885, 562), the difference in the boiling points of 20° previously noticed being due to a slight impurity present in Lellmann's base; the latter, when purified by means of the stannochloride, boils like γ-coniceïne at 173°. A direct comparison of specimens obtained by both methods also afforded complete proof of their identity.

In the previous paper it was left undecided which of the following formulæ represents γ-coniceïne,

$$CH_2<\substack{CH_2\cdot CH\\CH_2\cdot NH}>C\cdot CH_2\cdot CH_2Me, \quad \text{or} \quad CH_2<\substack{CH_2\cdot CH_2\\CH_2\cdot NH}>C:CH\cdot CH_2Me.$$

A compound of the first constitution should, on dehydrogenisation, readily yield propylpyridine, whereas the formation of this base could hardly be explained by the second formula. The authors therefore distilled the stannochloride of γ-coniceïne with zinc-dust, and purified the crude distillate by dissolving it in hydrochloric acid, extracting the non-basic portions with ether, adding excess of alkali, and distilling in a current of steam. The distillate was again dissolved in hydrochloric acid, and a little sodium nitrite added, and any nitrosamine formed removed by ether, the solution being then again made alkaline and distilled. In order to identify the base, it was converted into the platinochloride, the crystallographic examination of which gave results agreeing with those obtained by Ladenburg for propylpyridine platinochloride (*Annalen*, **247**, 20). The melting point was, however, found to be 172°, whereas Ladenburg found 159—160°. The authors, therefore, prepared a specimen of the platinochloride by Ladenburg's method, and found in this case also the melting point 172°. As this compound was investigated with great care by Ladenburg, the platinochloride must exist in two isomeric forms of different melting point, which, however, differ only very slightly in their crystallographic properties. The properties of the free base agree well with those given by Ladenburg and Hofmann for propylpyridine, and there can, therefore, be no doubt as to its identity with this compound, from which it

follows that γ-coniceïne has the first of the formulæ given above. This result also renders it probable that the secondary piperideïne bases obtained by Ladenburg in a similar manner from α-methyl-, α-ethyl-, and α-isopropylpiperidine have a corresponding constitution.

γ-Coniceïne appears to be also formed, together with conyrine, by the distillation of coniïne hydrochloride with zinc-dust.

When γ-coniceïne is reduced with tin and hydrochloric acid, it is readily converted into inactive coniïne. Its boiling point was found to be 165—166°, whilst its hydrochloride melted at 213°, whereas Ladenburg found the melting point to be 202—203°. It appears that the treatment with tin and hydrochloric acid exerts a purifying influence on the base, as dextro-coniïne hydrochloride, for which the authors, in agreement with Ladenburg, found the melting point 218°, after treatment with these reagents melted at 221°. H. G. C.

By-product from the Synthesis of Cocaïne. By C. Liebermann and F. Giesel (*Ber.*, **23**, 926—929).—A direct comparison of the compounds of the base described by the authors as methylcocaïne (this vol., p. 647) with those of Einhorn and Marquardt's dextrorotatory cocaïne (this vol., p. 646) has shown that the two bases are very probably identical. The nitrates of both compounds have the same solubility in water, namely, 1·55 in 100 at 20°. Dextrorotatory cocaïne, purified by means of the nitrate, melts at about 43—47°; the hydrochlorides of the two bases also melt within about 3° of one another.

Dextrorotatory benzoylecgonine hydrochloride, prepared from dextrorotatory cocaïne, is identical with the compound prepared from "methylcocaïne;" both substances form rhombic crystals $a : b : c = 0·8361 : 1 : 0·5184$.

The nitrates of dextrorotatory benzoylecgonine and "methylcocaïne" are equally soluble in water (about 1·1 in 100 at 19°). The methyl-derivative of "methylcocaïne" melts at the same temperature (115°) as the methyl-derivative of dextrorotatory ecgonine, and both have the same rotatory power. F. S. K.

Aricine. By H. Moissan and E. Landrin (*Compt. rend.*, **110**, 469—471).—The alkaloïd which was discovered by Pelletier and Coriol was obtained from the bark known as *Arica* or *Cusco quinquina*. The bark used by the authors contained 3·0 to 3·5 per cent. of the alkaloïd, a proportion much larger than that found by previous investigators. It was roughly powdered, mixed with 10 per cent. of lime and 10 per cent. of sodium hydroxide solution of 40°, and the mixture partially dried on a water-bath. It was then exhausted with ether, and the ethereal solution mixed with dilute sulphuric acid, which precipitated aricine sulphate. The sulphate was dissolved in boiling water, and the alkaloïd precipitated with ammonia and purified by repeated recrystallisation from alcohol. It has the composition $C_{23}H_{26}N_2O_4$, as stated by Gerhardt and by Hesse, melts at 188—189°, and is insoluble in water, but dissolves in alcohol (1 part in 100 at 15°, and 9 parts in 100 of the boiling solvent), and in ether (3 parts in 100 at 15°).

Its rotatory power in alcoholic solution is $[\alpha]_D = -58° 18'$, and in ethereal solution $[\alpha]_D = -92° 30'$. Contrary to the usual statements, the hydrochloride is optically active, its rotatory power having a sign opposite to that of the bases, $[\alpha]_D = +14° 30'$ in an alcoholic solution.

Aricine is distinguished from its isomeride cusconine by its melting point and rotatory power. The quantity of bark used was so great that 2 kilos. of aricine were obtained. The product was identical in properties with the aricine isolated by Pelletier. C. H. B.

Action of Resorcinol on Egg Albumin. By J. ANDEER (*Chem. Centr.*, 1890, i, 324; from *Arch. path. Anat.*, **119**, 191—192).—If a drop of egg albumin is allowed to fall into a saturated solution of resorcinol, the drop of albumin, at first transparent, becomes gradually opaque, and finally white like a hailstone. It gradually falls through the liquid, lengthens itself out to a band, becomes broader and broader, finally reaching the bottom. It has the appearance of a bacteriological culture. If the liquid is now shaken, it falls to the finest powder, and is so disseminated in the froth that it appears to have dissolved. The same effects are produced however dilute the egg albumin may be. J. W. L.

Reactions of Albumoses and Peptone. By R. NEUMEISTER *Zeit. Biol.*, **26**, 324—347).—The various reactions (biuret reaction, precipitation by nitric and other acids, and by ammonium sulphate and other salts) of the products of proteolysis are described and compared with one another (compare Abstr., 1888, 509, 516). Statements made by other observers in relation to their delicacy and applicability are reviewed and criticised.

The term *tryptophan* is suggested for the substance which is formed during pancreatic digestion from proteïds, and which gives a reddish-violet coloration with bromine. W. D. H.

Proteïnchrome and Proteïnchromogen. By E. STADELMANN (*Zeit. Biol.*, **26**, 491—526).—It has been known since the researches of Gmelin, Bernard, and others of the earlier physiologists that on tryptic digestion a substance is formed from proteïds which gives with chlorine, or better with bromine (not with iodine), a reddish-violet coloration. Other methods of decomposing proteïds, such as putrefaction, barium hydroxide, and strong (5 per cent.) sulphuric acid, give rise to many substances, among which this hitherto unnamed material is to be fonnd. It is not formed during gastric digestion. Krukenberg (*Verhandl. physik. med. Ges. Würzburg*, **18**) and Hemala (*Chem. Unters. wiss. Med.*, von C. F. W. Krukenberg, Heft 2) have previously investigated this substance, and Nencki (this Journal, 1875, 479) considered that it was probably identical with naphthylamine, a view which Hemala showed to be untenable. Neumeister (preceding abstract) has recently suggested the name tryptophan for it; the name here suggested is that of *proteïnchromogen* for the original substance, and of *proteïnchrome* for the coloured material formed on the addition of chlorine or bromine.

Proteïnchromogen dialyses through parchment paper, will not dis-

solve in ether or chloroform, is non-volatile, and is destroyed at 100°. It is precipitable by silver nitrate, and causes reduction of this salt in the cold. The pigment itself (proteïnchrome) is soluble in the digestion fluid, and is soluble in ether and in chloroform, the solutions showing a well-marked absorption-band at D. The halogens appear to be in a state of chemical combination with the organic radicle. Impure nitric acid destroys it. Many of these facts were previously described by Krukenberg, who considers that the substance is not a proteïd, but a member of the indigo-group.

Proteïnchromogen is stated by Neumeister to be soluble in amyl alcohol, and can thus be isolated. In the present research, amyl alcohol was not found to be at all a suitable reagent to employ for this purpose. In fact no method was found which would satisfactorily separate it from peptone, with which, in diffusibility and many of its reactions, it agrees closely, and from the amido-acids. The preparation of proteïnchrome by the use of 90 per cent. alcohol (for full details the original memoir must be consulted) met with better success. Its colour and other reactions show that it is not identical with naphthylamine. When dissolved in ether, it shows a well-marked absorption-band in the green (68—93); when dissolved in alcohol, the band does not appear until after the addition of sodium hydroxide; after treatment with various reagents, and in different solvents, the spectroscopic appearances differ, the measurements being given in detail.

Elementary analysis of several specimens gave the following percentage results:—

N.	Br.	S.	C.	H.	O.
10·99—11·92	19·77—23·16	2·95—3·77	48·12—51·34	4·45—5·28	8·03—12·00

From these numbers it is calculated that the percentage composition of proteïnchromogen is: C, 61·02; H, 6·89; N, 13·68; S, 4·69; and O, 13·71.

Proteïnchromogen is not formed from anti-products of digestion, but only from the hemi-group (hemi-peptone). It is thus a substance which must be classed with leucine, tyrosine, and similar materials formed during pancreatic digestion. Its reactions and general composition seem to point to its being a proteïd, or a substance allied to a proteïd; its high percentage of sulphur quite excludes the view that it belongs to the indigo-group.

W. D. H.

Melanin. By J. Brandl and L. Pfeiffer (*Zeit. Biol.*, 26, 348—376).—The pigment of melanotic tumours has been previously investigated by Berdez and Nencki (Abstr., 1888, 976), and by Mörner (Abstr., 1887, 168). In the present research, the material was obtained from a patient who died of melano-sarcoma of the liver. Details of the clinical history of the case and autopsy are briefly given.

The pigment was separated from the proteïds of the tumour by the method of Berdez and Nencki, and was found to be insoluble in most reagents; concentrated mineral acids dissolve it slowly in the cold, more quickly when warmed; iron is then found in the acid, showing that it has decomposed the pigment. In concentrated alkalis in the cold it is almost insoluble; on the application of heat, it dissolves with the formation of a sulphide of the alkali. Dilute potassium hydroxide (1 per cent.) dissolves it slightly, forming a dark-red solution. It is precipitated from this solution by a solution of magnesium sulphate, or of barium chloride, or by neutralisation.

Specimens of the pigment submitted to elementary analysis gave percentage results which may be compared with the results of previous observers in the following table:—

	Nencki and Berdez.			Mörner.		Brandl and Pfeiffer.
	Phymatorusin.	Hippomelanin.		Insoluble in acetic acid.	Soluble in acetic acid.	
		a.	*b*.			
C....	53·48	53·6	55·61	55·72	—	53·87
H....	4·03	3·88	3·82	6·00	—	4·20
N....	10·55	10·48	10·87	12·30	—	10·56
S....	10·67	2·84	2·81	7·97	5·90	3·63
Fe...	—	—	—	0·07	0·21	0·52
O....	21·27	29·20	26·89	17·94	—	27·25

The preparations made in the present research were, after removal of the iron, found to be free from ash.

In agreement with Mörner, and in opposition to Berdez and Nencki, it is considered probable that melanin originates from hæmoglobin; during the course of the disease, as the tumour grew in size, the number of red corpuscles and the percentage of hæmoglobin in the blood fell steadily.

The urine of patients suffering from melanotic disease contains, as a rule, a dark pigment, or a chromogen (melanogen) which is converted into the pigment by oxidation. Many observers have considered that this pigment is the same as that occurring in the tumours. The quantity of urine available for research in the present case was too small to make a thorough and systematic analysis. It, however, became dark-brown or black on exposure to the air, or by oxidising in other ways. With bromine-water, a minimal quantity of a brownish-black precipitate was obtained. Zeller has stated that this substance, which he calls bromomelanin, contains 16·6 per cent. of bromine (*Langenbeck's Arch. klin. Chirurg.*, **29**, 245). An amyl alcohol solution of the pigment separated from the urine gave two absorption-bands in the yellow-green and blne-green regions of the spectrum respectively, and, on ignition, yielded an ash that contained iron.

W. D. H.

Neurokeratin. By W. KÜHNE and R. H. CHITTENDEN (*Zeit. Biol.*, **26**, 291—323).—Neurokeratin, the supporting framework of nervous tissue, may be separated from other constituents of that tissue by its extreme insolubility in various reagents; it is also unaffected by the gastric and pancreatic ferments.

In the present research, the tissue was in some cases submitted to artificial digestion before, in other cases after, the lecithin and cholesterin were removed by protracted extractions with alcohol and ether. Five specimens were thus prepared and subjected to elementary analysis, and the mean percentage result compared with those similarly obtained from keratin (prepared from hair) are as follows:—

	C	H.	N.	S.	O.
Keratin	49·45	6·52	16·81	4·02	23·20
Neurokeratin..	56·99	7·54	13·15	1·87	20·45

A few estimations were made of the quantity of neurokeratin in various parts of the nervous system by weighing the residue of a weighed amount of the tissue after treatment with numerous reagents in which the albumin, cholesterin, lecithin, nucleïn, and other constituents of that tissue are soluble. The percentage amounts found were as follows:—

1. Nerve (brachial plexus)	0·316
2. Cerebellar cortex	0·312
3. White matter of cerebrum................	2·243
4. White matter of corpus callosum	2·902
5. Cerebral cortex..........................	0·327
6. Nerve (brachial and sciatic)	0·601
7. White matter of corpus callosum	2·572

The most noteworthy point in connection with these analyses is the remarkably high percentage of neurokeratin in white matter.

Liver and kidney treated in the same way only gave an imponderable residue.

The paper concludes with an account of the microscopic appearances of neurokeratin in the nerve-fibres before and after they had been treated with the various reagents used. W. D. H.

Physiological Chemistry.

Living Motors and the Theory of Heat. By R. LEZÉ (*Ann. Agron.*, **16**, 30—38).—The author draws a comparison between the useful effect of the food supplied to a working horse and that of the food consumed by heat engines, based on the following figures. The albuminoïds of food are estimated to furnish 4,000 calories per kilogram on combustion; fats, 10,000 calories per kilo.; carbohydrates

and woody fibre, 4,000 calories per kilo. Taking a horse weighing 700 kilos., and consuming per diem 7 kilos. lucerne hay, 10·5 kilos. maize, 3·9 kilos. bran, and 7 kilos. straw, the calorific value of the food will be (leaving the straw out of account)—

		calories.
From albuminoïds................	2·807 × 4,000 =	11,228
„ fatty matter................	1·092 × 10,000 =	10,920
„ carbohydrates and woody fibre	14·000 × 4,000 =	56,000
		78,148

There is thus expended on the horse 80,000 calories per diem, the same amount as is furnished by complete combustion of 10 kilos. of carbon. Such a horse will accomplish 2,700,000 kilogrammetres of work per day of 10 hours; and, admitting 1 kilo. of carbon per steam horse power per hour, the 10 kilos. of carbon burnt under a steam-engine will do the same. In the steam-engine, as in the horse, this is only one-thirteenth of the theoretical equivalent, namely, 80,000 × 425 = 34,000,000 kilogrammetres. But with heat-engines there is the prospect of indefinite improvement in the duty, whereas there is no such prospect in the case of animals. Pursuing the comparison, the heat-engine works at an elevated temperature, the horse not above 38°, and its weight is only one-sixth to one-eighth that of the horse. Supposing the horse to lose 15,700 calories per day by radiation, there remains 58,950 disposed of in other ways, since the work accomplished only requires 6,350. This quantity of 58,950 calories is partly used up in the phenomena of life and partly represented by unburnt fuel in the excretions. The heat corresponding with the carbonic anhydride expired, accounts for but a small part, about 4,400 calories. The combustion of the fuel is much less complete in the animal than in our furnaces; the reactions are more complex—more difficult to follow; the animal mechanism is so organised that the falls of temperature are hardly sensible, and the equilibrium soon restored. In the heat-engine, the consumption of fuel is directly proportional to the work done, whereas the animal consumes fuel when doing no work. J. M. H. M.

The Difference between Arterial and Venous Blood in different Blood-vessels. By F. KRÜGER (*Zeit. Biol.*, **26**, 452—490).—Previous researches on this subject are first epitomised. In the present research, the experiments were made exclusively on cats; the results obtained being as follow:—

1. The amount of dry residue and of hæmoglobin in the blood of the carotid artery and jugular vein is the same.

2. After the slightest passive congestion has occurred in any vascular area, both dry residue and hæmoglobin are increased in the blood drawn from that region.

3. The percentage of hæmoglobin and of solid residue in the blood of the afferent and efferent vessels of the liver is usually different, but no constant relation exists between the two.

4. The blood of the larger mesenteric vein is poorer in both total

solids and hæmoglobin than that of the portal vein and of the splenic vein.

5. The blood of the splenic vein is generally richer in hæmoglobin and in solid residue than that of the arterial blood. There are occasional exceptions to this rule. The amount of fibrin in arterial and venous blood is approximately equal. The specific gravity of the defibrinated blood is sometimes higher in the splenic vein, sometimes in the artery. The specific gravity of the serum is, on the contrary, always higher in the artery than the vein; the same is true for the solid residue.

6. Hæmoglobin appears to be both formed and destroyed in the spleen.

7. The blood of the renal vein is poorer in both hæmoglobin and solid residue than the arterial blood. The amount of fibrin is also less in the blood from the kidneys than in arterial blood. The dry residue and specific gravity of both defibrinated blood and of the serum of the venous blood from the kidney is always smaller than in that from arterial blood. There appears to be little doubt that blood pigment is destroyed in the kidneys.

The hæmoglobin estimations were made by means of Hüfner's spectrophotometer. W. D. H.

The Permeability of the Red Corpuscles in relation to their Isotonic Coefficients. By H. J. Hamburger (*Zeit. Biol.*, **26**, 414—433).—When defibrinated blood is mixed with salt solutions of different concentration, and the corpuscles allowed to subside, it is found that there is for each salt a certain concentration when no hæmoglobin is dissolved out from the red corpuscles, while a saline solution of less concentration becomes tinged with the pigment. The mean of these two limits was found to give numbers identical with the isotonic coefficients of H. de Vries (*Pringsheim's Jahr. wiss. Botanik*, **14**, Heft 4).

The salt solutions in which the corpuscles lose their pigment are, in water-attracting power, far inferior to the serum in which they are contained. It is, therefore, necessary to add at least 50 per cent. of water, after admixture with the defibrinated blood, before the corpuscles allow their pigment to be removed. The salt solutions which have the same water-attracting power as the serum are designated isotonic, with one higher than that of the serum, hyperisotonic, with one lower, hypisotonic.

The present experiments were performed on the blood of the ox, horse, and pig; and the substances investigated were solutions of potassium nitrate, magnesium sulphate, sodium chloride, sodium sulphate, cane-sugar, dextrose, and diluted serum: the results obtained may be summed up as follows:—

1. That the blood corpuscles of defibrinated blood are exceedingly permeable by salts.

2. That after the addition of isotonic, hyperisotonic, and hypisotonic solutions of salts, sugar, and serum to defibrinated blood (which is diluted with water before the admixture), a passing out of certain constituents of the corpuscles into the surrounding medium occurs;

this takes place in such a manner that the water-attracting power of neither undergoes any change, or in other words in isotonic proportions. W. D. H.

Blood of the Aplysiæ. By L. Cuénot (*Compt. rend.*, **110**, 724—725).—The blood from the heart of *Aplysia depilans* has a distinct rose colour, due to the presence of 0·636 per cent. of an albuminoid which is precipitated by alcohol, acids, mercuric chloride, and the usual reagents. Its colour has no relation to the presence of oxygen, and it seems improbable that it plays any part in respiration. When the blood is dialysed, or exposed for a long time to air, it decomposes spontaneously, part of the albuminoïd remaining in solution and part separating in a white, flocculent form. This albuminoïd is distinct from hæmocyanin and may be called *hæmorhodin*. If the blood is concentrated in a vacuum and heated, it becomes opalescent at 58°, and seems to coagulate completely at about 70°.

The blood of *Aplysia punctata* is quite different, and contains 1·77 per cent. of a perfectly colourless hæmocyanin which is not affected by air and coagulates at about 76°. This albuminoid probably plays no part in the absorption of oxygen. C. H. B.

Presence in Chyle of a Ferment which destroys Sugar. By R. Lépine Compt. rend., **110**, 742—745).—The removal of the pancreas of a dog was followed by intense diabetes, the ratio of sugar to urea rapidly increasing and becoming as high as 233 : 100. The injection of chyle into the jugular vein caused a very marked reduction in the amount of sugar, the ratio of sugar to urea, four hours afterwards, being 24 : 100. After a time, however, the diabetes returned. A similar, but smaller, reduction in the quantity of sugar was caused by the intravenous injection of malt diastase. The addition of chyle to a 1 per cent. solution of glucose kept at 38° caused a decided reduction of the amount of glucose in the liquid.

From these facts, the author concludes that the chyle contains a ferment which destroys glucose, and that one of the functions of the pancreas is to provide the body with this ferment, and thus prevent the abnormal accumulation of glucose. Diabetes seems to be a consequence of an insufficient supply of the ferment. C. H. B.

The Formation and Fate of Glycogen. By W. Prausnitz (*Zeit. Biol.*, **26**, 377—413).—The experiments described were made on hens; a period of four days' hunger was found sufficient to reduce the quantity of glycogen in the body to a *minimum*. As starch was found to be almost indigestible, the animals were then fed on a known quantity of cane-sugar, and killed a certain number of hours after feeding. The amount of cane-sugar which remained unaltered, or of dextrose into which it had been converted, in the alimentary canal was then ascertained; this amount subtracted from the dose given, gave the amount absorbed; the amount of glycogen in the whole body was then ascertained.

An example of one of the numerous experiments performed may be taken as a sample of the data found.

Experiment 7.—After four days' hunger, the hen lost 14·17 per cent. of its original weight. It was then fed with 24·35 gram of cane-sugar, and killed 48 hours afterwards.

No sugar was found in the stomach contents: the fæces contained 1·5 gram, the animal had in its liver 0·022 gram of glycogen; the rest of the body, 0·484 gram of glycogen. The total glycogen (0·506 gram) corresponds to 0·534 gram of cane-sugar. 22·85 grams of sugar had therefore been absorbed, and of this 2·33 per cent. was found in the form of glycogen. The relation of glycogen to total body-weight (excluding feathers and intestinal contents) was 0·048 : 100. The relation of the hepatic glycogen to that in the rest of the body was 1 : 22.

This experiment, on being compared with others of a similar kind, but differing from it in the length of time intervening between the feeding and the killing of the animal, shows certain results which are represented in the form of curves, and which may be briefly stated as follows:—The amount of total glycogen in the body, in the liver, and in the muscles, runs closely parallel to one another; the maximum of glycogen formation as evidenced by the quantity found after death occurs 20 hours after feeding; the curves rise to this point, and then fall. This is is somewhat later than is stated by previous observers, and is certainly not coincident with the maximum of bile-formation.

Some observers consider that the liver is the exclusive seat of the formation of glycogen; and that glycogen in the muscles and elsewhere is derived from the liver; other physiologists maintain that other cells besides liver cells may have a glycogenic function. In the present research it was found that the blood contains no trace of glycogen, so that if that substance is transported from the liver, it must pass in some soluble form. It is, however, considered probable that the liver is not the only seat of glycogenesis.

The paper concludes with the results of a few experiments on what happens to the glycogen of muscles after death. It is maintained in opposition to Böhm (*Pflüger's Archiv*, **23**, 44), that the muscle glycogen rapidly disappears after death. W. D. H.

Absorption of Different Fats from the Alimentary Canal. By L. Arnschink (*Zeit. Biol.*, **26**, 434—451).—It is very generally believed that fats with a high melting point are not so digestible as those which are liquid at the body temperature. The object of the present research was to put this question to the test of accurate experiment, feeding a dog with a weighed quantity of a fat, and ascertaining the amount which is not absorbed, by analysing the fæces.

The following table gives succinctly the principal facts found :—

Fat given.		Composition. Oleïn per cent.	Composition. Solid fats per cent.	Melting point of fat.	Fæces. Neutral fat per cent.	Fæces. Fatty acids per cent.	Fæces. Soaps per cent.	Fæces. Total fatty matter in the day. Grams.	Amount of fat not absorbed. Per cent.
	grms.			°					
Stearin..	20	0	100	60	93·0	0	7·0	18·2	91·0
" ..	20	0	100	60	94·8	0	5·2	17·2	86·2
Pig's fat.	100	52	48	34	26·6	19·8	58·6	2·8	2 8
Mutton suet .	100	30	70	49	41·2	51·4	7·4	7·4	7·4
Goose fat	50	71	29	25	36·7	55·4	7·9	1·2	2·5
Olive oil.	50	72	28	0	52·6	23·3	24·0	1·1	2·3
Mixture of stearin and almond oil	20	54	46	55	60·6	19·4	20·0	2·2	10·6

This clearly shows that the melting point and the amount of fat absorbed vary in the way already supposed. The bearing of this on diet in cases of stomach disease is pointed out. W. D. H.

Behaviour of Sulphur in the Organism, and the Detection of Thiosulphuric acid in Urine. By W. PRESCH (*Chem. Centr.*, 1890, i, 405—406; from *Arch. path. Anat.*, **119**, 148—167).—The author has used Salkowski's method for the detection of thiosulphuric acid in urine, which depends on the fact that if the substance is distilled with hydrochloric acid, free sulphur collects in the condenser, whilst hydrogen sulphide is evolved. When applying this test, the urine was tested for hydrogen sulphide first, and in its absence, any formation of hydrogen sulphide may be attributed to the presence of thiosulphuric acid. Another delicate test is to precipitate any thiosulphuric acid as silver thiosulphate; the latter is decomposed on heating into silver sulphate and sulphide, the former being then tested for. The author could not detect the least trace of thiosulphuric acid in any healthy urine. Experimenting on himself on the effect of taking sulphur in the form of flowers of sulphur, he found that 73·5 per cent. was excreted as sulphuric acid, and that the remainder is absorbed for the formation of organic sulphur compounds.
J. W. L.

Composition of the Milk of the Bottle-nose Whale. By P. F. FRANKLAND and F. J. HAMBLY (*Chem. News*, **61**, 63).—The authors obtained the following results from a small sample of milk from the bottle-nose whale; the numbers are per cent.:—

Total solids (100—105 C.)	51·33
Water............................	48·67
Solids not fat.....................	7·57

Fat	43·76
Ash	0·46

The ash is rich in phosphoric acid, and the fat contains a large proportion of difficulty saponifiable fat (m.p. 51°) presumedly spermaceti.

D. A. L.

Physiological Action and Optical Properties of Inorganic Substances. By J. BLAKE (*Zeit. physikal. Chem.*, **5**, 217—220).—The author, in amplification of a former paper (*ibid.*, **2**, 769), here discusses the parallelism between the physiological action of inorganic substances and their optical behaviour, together with the factors of moment in determining these properties—namely, isomorphism, valency, and atomic weight.

Substances of one isomorphous group have in general the same physiological action; in an investigation of 44 elements, the only exceptions to this rule (nitrogen and potassium), were found to be also exceptional with regard to their spectra and general optical activity. Within an isomorphous group, increase of molecular weight (or, more probably, of molecular volume) conditions increased physiological activity. The influence of valency is such as to determine the sphere of the action; thus bivalent elements act on a greater number of nerve centres than univalent elements, trivalent on more than bivalent, and so on. The author draws attention to the connection between the valency of hydrogen, oxygen, and nitrogen and the nature of their spectra. The above relations hold most strictly for electro-positive elements.

J. W.

Action of Related Chemical Compounds on Animals. By W. GIBBS and H. A. HARE (*Amer. Chem. J.*, **12**, 145—152)—A continuation of a research, for the first part of which see this vol., p. 280; experiments with the cresols form the subject of the present paper. These all act as sensory and motor paralysants. The ortho- and para-compounds act as stimulants to inhibitory processes; the meta-compound has no such influence. The ortho-compound seems to be the more powerful inhibitory stimulant of the two, and is the most powerful cardiac depressant of the group. After orthocresol in this respect comes paracresol; metacresol having little cardiac influence comparatively; thus, ortho-cresol kills when injected in the strength of 0·08 gram per kilo. of body-weight, paracresol in the dose of 0·1 gram per kilo., and metacresol when the amount equals 0·15 gram per kilo. Metacresol seems to affect the vaso-motor system more than paracresol, but probably not more than orthocresol. Orthocresol and paracresol are grouped as inhibitory stimulants and cardiac depressants; orthocresol and metacresol as vaso-motor depressants. On the nervous system of the frog these compounds act as a paralysants in the same order as they act on the heart. Thus, of orthocresol 0·004 gram per kilo. of body-weight paralyses the nerves and causes death. Paracresol kills at 0·006 gram, and metacresol only at 0·044 gram per kilo.

C. F. B.

Chemistry of Vegetable Physiology and Agriculture.

Effect of Copper Salts on Elliptical Yeast. By A. ROMMIER (*Compt. rend.*, **110**, 536—539).—Grapes from wines which had been treated with solutions of copper salts for the prevention of mildew, either did not ferment at all or fermented in consequence of the development of the species of yeast known as *apiculatus*. The ordinary elliptical wine-yeast did not develop. Direct experiments showed that 0·075 to 0·100 gram of copper in the form of sulphate per 1000 c.c. greatly retarded fermentation by elliptical yeast. It is highly probable, therefore, that the copper salts will exert a similar influence on the sporulation of this yeast on the skin of the grape, but will not prevent the deposition of other yeasts through the agency of insects.

The absence of elliptical yeast will not exert any marked influence in the case of common wines, but will be decidedly injurious when it is required to produce wines of fine bouquet. The use of copper salts should, therefore, be avoided as far as possible. C. H. B.

The Fixation of Free Nitrogen. By Sir J. B. LAWES and J. H. GILBERT (*Proc. Roy. Soc.*, **47**, 85—118).—In a previous paper (*Phil. Trans.*, 1889, 1—107) the authors discussed the history and present position of the question of the sources of the nitrogen of vegetation. The earlier Rothamsted results, as well as those of Boussingault, obtained under conditions which excluded the action of electricity and of microbes, pointed to the conclusion that the higher chlorophyllous plants have not the power of taking up elementary nitrogen. It was concluded that atmospheric nitrogen is not a source of nitrogen in the case of gramineous, cruciferous, chenopodiaceous, or solaneous crops, but with regard to the *Leguminosæ* it was admitted that there was not sufficient evidence to account for the whole of the nitrogen taken up. Of the recent researches bearing on the subject, those of Hellriegel and Wilfarth (Abstr., 1889, 640; and *Ber., botan. Ges.*, **7**, 138) were considered the most conclusive, and in 1888 experiments, on similar lines to Hellriegel's, were commenced at Rothamsted. The plants selected were peas and blue and yellow lupins, but only the peas gave very definite results. There were four pots, each with three pea plants, as follows:—No. 1. Washed sand (9 lbs.), containing a little nitrogen (0·0027 per cent.), and provided with the necessary ash constituents. Nos. 2 and 3. The same prepared sand seeded with soil organisms. No. 4. Garden soil from which the soil extract added to Nos. 2 and 3 was made. About five or six weeks after sowing, the plants of pots 2 and 3 acquired a darker colour than those of pot 1, and from this time the plants (pots 2 and 3) gained both in leaf surface and in number of leaflets, and maintained their brighter green colour. At the conclusion of the experiment it was found that the roots of all the plants had nodules, but that those of the plants of the seeded pots were much larger and more abundant

than those of pot 1. The fact that the plants of this pot had nodules at all is attributed to the impurity of the sand, and its not having been sterilised. The roots of the plants grown in garden soil showed comparatively few nodules, which were, moreover, smaller than those of the other pots. None of the plants flowered, owing to the lateness of the season.

The following table shows the amount of dry produce (including roots), and the amount of nitrogen contained in it, as well as the nitrogen of the seeds sown, and the initial and final nitrogen of the sand and soil :—

	Dry produce.	Nitrogen								
		At commencement.			At conclusion.			Gain.	In total products; total initial = 1.	In plants, nitrogen in seed = 1.
		In soil.	In seeds sown.	Total.	In soil.	In produce.	Total.			
	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.
Pot 1	10·023	0·0999	0·0293	0·1292	0·1096	0·2822	0·3918	0·2626	3·03	9·63
Pot 2	11·777	0·0999	0·0298	0·1297	0·0974	0·5361	0·6335	0·5038	4·88	17·99
Pot 3	11·159	0·0999	0·0291	0·1290	0·0848	0·4357	0·5205	0·3915	4·04	14·97
Pot 4	15·634	7·9989	0·0301	8·0290	7·9989	0·6600	8·6589	0·6299	1·08	21·93

The amount of nitrogen in the 25 c.c. of soil extract, added to pots 2 and 3, is so small (0·790 milligram) that it need not be taken into account. Whilst the amount of dry produce was only slightly increased by the application of soil organisms, the amount of nitrogen was nearly doubled. With regard to pot 4, the results indicating a gain of nitrogen are not to be considered as conclusive, owing to the difficulty of detecting slight changes in the amount of nitrogen in a large bulk of rich soil. This experiment was, in fact, intended more to compare the growth with that of the other pots, than for exact quantitative estimates of gain or loss. There is no evidence to show that either the sand or soil has taken up nitrogen on its own account.

The experiments of the second season included peas, red clover, vetches, blue and yellow lupins, and lucerne. The sand used was a coarse, white sand, which was washed, and sufficiently, if not absolutely, sterilised, by heating for some days at nearly 100°. The necessary ash constituents mixed with an equal weight of calcium carbonate were added to each pot. There were four pots to each series. No. 1 contained the prepared sand alone; Nos. 2 and 3 the same sand, to which a soil extract was added, prepared from a lupin sandy soil for the lupins, and from a garden soil for all the rest. No. 4 garden soil, or for lupins the special lupin soil. The peas and vetches of the unseeded pots were very limited in growth, whilst those of the second and third pots grew luxuriantly, being taller even

than those grown in garden soil. On the other hand, the latter were more vigorous and produced flower and seed. The results obtained with yellow lupins were stili more striking. Whilst the plants of pot 1 barely appeared above the rim of the pot, those of pots 2 and 3 were large, branched plants, the largest being 2 feet high, which flowered and seeded freely. The plants grown in the lupin soil were considerably smaller, which may be due to the fact that the lupin soil was much less porous than the sand of the other pots. The roots of all the plants (peas, vetches, aud lupins) grown in sand without soil extract seeding were, like the plants, of very limited development, and were entirely free from modules; in pots 2 and 3, of each series, the root development was very great, and the roots showed an abundance of nodules. In the garden soil and the lupin soil the root development and nodule formation were much less.

The blue lupins failed, with one exception, and the clover and lucerne are left for further growth.

The results confirm those of Hellriegel and Wilfarth in showing the fixation of free nitrogen under the influence of microbe seeding, and the resulting nodule formation on the roots of the leguminous plants. Hellriegel agrees with the authors that the *Leguminosæ* utilise soil nitrogen, and he considers that the soil would be drawn on first, and that this source is supplemented by the elementary nitrogen of the air, brought into combination by means of the organisms; he also considers that there would be more or less fixation even with a soil rich in nitrogen. On the other hand, Vines (*Annals of Botany*, **2**, 386) found that the formation of tubercles and presumably also the fixation of free nitrogen, is mnch reduced by the application of much nitrate; and the Rothamsted experiments indicate that with a rich soil, there are far fewer nodules formed than with a sand containing but little nitrogen and seeded with soil organisms.

Regarding the way in which the organisms, which, in symbiosis with the higher plants, bring about the fixation, much has yet to be learnt. The authors suggest the alternatives:—" (1.) That somehow or other, the plant itself is enabled, under the conditions of symbiotic life, to fix free nitrogen of the atmosphere by its leaves, a supposition in favour of which there seems to be no evidence whatever. (2.) That the parasite utilises and fixes free nitrogen, and that the nitrogenous compounds formed are taken up by the host. On such a supposition, the actually ascertained large gain of nitrogen by the leguminous plant growing in a nitrogen-free, but properly infected, soil becomes intelligible." (Compare Bréal, this vol., p. 79; Marshall Ward, *Proc. Roy. Soc.*, **46**, 431; and Prażmowski, *Landw. Versuchs-Stat.*, **37**, 162.) N. H. M.

The Nitrogen Question. By A. PETERMANN (*Bull. Stat. Agronom. Gembloux*, No. **47**, 1–17, 1890).—Yellow lupins were grown in vessels containing 1 cub. metre of washed, white sand (1400 kilos.). The air-dried sand contained 0·0400 per cent. of organic matter (with 0·0004699 per cent. of nitrogen) and 0·029 per cent. of nutritive mineral matter. The experiments were made in the open air; the rainfall and drainage through the sand and the nitrogen in the rain and drainage were

determined. There were six vessels, as follows:—(1) Sand alone; (2) sand with phosphatic slag and potassium and magnesium sulphates; (3) sand and minerals as in (2), and soil extract containing organisms; (4) sand and minerals with sodium nitrate (176·6 grams); (5) sand and minerals with ammonium sulphate (137·5 grams); (6) sand and minerals with dried blood (225·7 grams). The amount of nitrogen applied to vessels 4, 5, and 6 was in each case the same (27·6 grams). 36 seeds of *Lupinus luteus* were sown on May 2, and on July 30 plants of all the six vessels were in flower. In No. 1 nine plants died; the rest were small, with small flowers. Those of Nos. 2 and 3 were nearly identical in appearance, and were much stronger and larger than those of No. 1. The plants of vessels 4, 5, and 6 were much larger still, especially those of No. 6, which were all the time superior to any of the others. The less favourable result with sodium nitrate is attributed to its greater solubility and its consequent removal to the lower part of the sand out of reach of the shorter roots. Nodules were found on the roots in all six vessels.

The numerical results are shown in the following table:—

	Dry produce.	Nitrogen.							
		In produce.	In soil, final.	In drainage.	In seed sown.	In soil, initial.	In manure.	In rain.	Derived from air.
	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.
1...	68·4	0·8952	8·1648	0·2290	0 3338	6·5786	—	0·3456	+2·0310
2...	236·5	4·8453	8·1648	0 1764	0·3337	6·5786	—	0·3456	+5·9286
3...	223 5	4·6509	8·8900	0·2288	0·3393	6·5786	—	0·3456	+6·5062
4...	445·0	8·0459	11·4268	19·0254	0·3355	6·5786	27·600	0·3456	+3·6384
5...	447·8	8·0416	12·5146	12·8697	0·3285	6·5786	27·600	0·3456	−1 4268
6...	809·0	10·0044	14·3276	4·5196	0·3308	6·5786	27·600	0·3456	−6·0034

The results show that atmospheric nitrogen may, under certain conditions, contribute to vegetable growth, as in a soil poor in nitrogen and containing soil organisms; and, further, that sodium nitrate is not, as sometimes supposed, injurious to lupins, but is highly beneficial.

Nitrogen determinations made with root nodules show that these are richer in nitrogen than the rest of the plants to which they are attached.

In view of the results obtained by other investigators, indicating that cereals which have no root nodules acquire nitrogen from the air, and that the soil in which they are grown also becomes richer in nitrogen, the author would guard against exaggerating the physiological rôle of the tubercles. They cannot be the only cause of nitrogen fixation, although their presence may explain why the intervention of atmospheric nitrogen is most marked in the case of the *Leguminosæ*.

Further experiments will be made to decide the question whether it is the combined or the elementary nitrogen of the air which is utilised.

N. H. M.

Assimilation of Carbon by Green Plants. By E. H. ACTON (*Proc. Roy. Soc.*, **46**, 118—121).—Plants or shoots grown in a "culture liquid" were deprived of starch by placing them in an atmosphere free from carbonic anhydride, and were submitted to the action of the following substances:—Acraldehyde, acraldehyde-ammonia, the compound of acraldehyde with sodium hydrogen sulphite, allyl alcohol, glucose, acetaldehyde, aldehyde-ammonia, glycerol, levulinic acid, calcium levulinate, cane-sugar, inulin, dextrins, soluble starch, glycogen, extract of natural humus, and the humus-like product of the action of alkalis on cane-sugar. The following results were obtained:—Starch is formed when "soluble starch" is supplied to the leaves, but not when it is applied to the roots. "Extract of natural humus" forms starch when supplied to the roots, but not when supplied to the leaves. Glucose in 0·5 per cent. solution is more readily taken up when supplied to the roots than cane-sugar. The roots of plants can withdraw all the glucose from a 1 per cent. solution and remain healthy. The remaining substances did not produce starch. The author concludes that green plants cannot normally obtain carbon from organic substances, excepting carbohydrates; that they have lost their power of using organic compounds as a source of carbon; and that if a compound of an aldehydic nature is formed as an intermediate product between carbonic anhydride and water on the one hand and glucose on the other, it can only be polymerised at the moment of formation. H. K. T.

The Diffusion of Alumina in Plants. By L. RICCIARDI (*Gazzetta*, **19**, 150—160).—After giving a summary of the previous work on this subject, the author gives the following analyses, which were made with a view to trace the connection between the character of the soil and the amount of alumina absorbed by the plant, and to ascertain the distribution of the alumina in the parts of individual plants.

(1.) *Analyses of the Plants.*

	Aluminia in 100 parts of ash.
Twigs of vine from strongly aluminous soil (Bari)	0·850
„ „ calcareous „ „	0·810
„ from moderately calcareous soil (Bari)	1·140
Trunk and branches of "manderin orange" (Bari)	0·218
Peel and seeds of "manderin orange" (Bari)	0·093
„ „ „ (Cava dei Tirreni)	0·121
Leaves of "manderin orange"	0·022
Entire fruit of prickly pear (Bari)	0·063
„ „ „ from Catania (4)	0·092
Phyllodes „ „ (Bari)	0·148
„ „ „ from Catania (4)	0·167
Dry husks of almond (Bari)	0·695
„ nuts „ „	0·138
Pulp of the siliqua of *Ceratonia siliqua* (Bari)	0·503
„ „ „ „ from Catania (5)	0·607
Carob of *Ceratonia siliqua* (Bari)	0·062
„ „ „ (Catania)	0·064
Tobacco leaves from Cava dei Tirreni	2·151
White lupins	0·042

(2.) *Analyses of the Soils.*

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
SiO_2..	45·30	—	41·71	49·27	50·23	—	—	—	63·14	52·26
TiO_2..	—	—	—	0·75	0·31	—	—	—	—	—
CO_2..	10·50	44·68	—	—	—	47·15	47·02	47·16	—	—
P_2O_5.	0·32	—	0·75	1·21	3·16	—	—	—	0·09	0·94
SO_3..	trace	—	trace	0·05	0·08	—	—	—	—	0·22
Cl....	do.	—	do.	—	—	—	—	—	—	0·42
Al_2O_3.	14·20	—	20·28	16·33	15·55	—	—	—	17·34	16·99
FeO..	6·57	—	—	7·78	10·48	—	—	—	0·76	5·22
Fe_2O_3		—	13·03	4·79		—	—	—	4·10	2·13
MnO.	0·32	—	0·41		0·52	—	—	—	—	—
CaO .	12·30	50·16	3·59	12·53	11·73	34·84	32·64	33·84	5·91	6·64
MgO.	1·56	4·8	2·62	4·52	5·09	18·09	20·38	18·64	2·57	1·86
K_2O..	0·90	—	0·59	0·79	0·51	—	—	—	3·89	8·83
Na_2O.		—		1·65	2·78	—	—	—	1·58	1·63
Insol..	—	0·36	—	—	—	—	—	0·47	—	—
Water	8·03	—	17·02	—	—	—	—	—	—	—
Sp. gr. at 18°	2·24	2·623 at 16°	2·14	2·839	2·811	—	—	—	—	—

The soil in the neighbourhood of Bari, Ruvo, &c., is formed by the disintegration of the marly clay (1), of a limestone belonging to the cretaceous formation (2), and of a ferruginous earth (3).

The soil in the neighbourhood of Catania consists of the decomposed lava of 1669 (4), and of the lava (5). The soil at Cava dei Tirreni consists of a mixture of the detritus of the Apennine limestones (6), (7), (8), with the volcanic rocks (9) and (10).

From the above analyses, the author concludes that the assimilation of alumina does not depend on the percentage contained in the soil, and that, generally speaking, alumina is most abundant in the trunk and branches of a plant, less so in the husks and seeds, and least of all in the leaves. S. B. A. A.

Organic Acids in the Sorghum Cane. By H. W. Wiley and W. Maxwell (*Amer. Chem. J.*, **12**, 216).—Preliminary investigations of the juice of the Sorghum cane have shown that it contains the following acids in the following order by proportion:—Aconitic, citric, malic, oleic, and formic acids, with decreasing amounts of tartaric, oxalic, and acetic acids, traces only of the last two being present. The authors are awaiting the next season in order to obtain a fresh supply of material. C. F. B.

Function of Tannin in Plants. By M. Büsgen (*Chem. Centr.*, 1890, i, 397—398; *Jena. Zeit.*, **24**, 11—60).—From investigations conducted by the author, he draws the conclusion that tannin continually disappears during the life of plants, and both from those cells such as young cork cells and those of the bark, which die rapidly, as also from those such as the roots of the triticum family, which have a longer term of life. Primary and secondary tannins behave not altogether differently, and these are not necessarily produced in a different

manner. Tannin, like starch, appears to be formed just at those parts where there is an abundance of materials present necessary for its production.

On the other hand, whilst starch is used by the plant for the further building up of its structure, there is no proof that tannin is put to this use. J. W. L.

Tannin in Indian and Ceylon Teas. By D. HOOPER (*Chem. News*, **60**, 311—312).—The tannin in various samples of tea was estimated by precipitation with lead acetate, and the tabulated results indicate that the quantity present was not influenced either by the quality of the tea or by the altitude at which it was grown. Tannin constitutes the "strength" of the tea, and, with 1 part of tea to 100 of boiling water, about 30 per cent. of the tannin in tea is extracted by water in 5 minutes, and about 50 per cent. in 10 minutes.

D. A. L.

Experimental Plots at Grignon in 1889. By P. P. DEHÉRAIN (*Ann. Agron.*, **16**, 1—29).—*Potatoes.*—Excellent results were obtained with Richter's Imperator, which was tried against Van der Veer and Chardon, the best plots of each yielding 33,150, 28,450, and 28,200 kilos. per hectare respectively. The starch contained in these crops amounted to 8,218, 5,498, and 5,234 kilos. respectively. The proportion of small tubers was 8 per cent. in Richter's Imperator, 12 in Chardon, and 13 in Van der Veer. The different sized sets produced no sensible differences in the crops. The greatest profit was shown by the plot not manured in 1890, but receiving 50,000 kilos. farmyard manure and 200 kilos. ammonium sulphate per hectare in the previous year.

Sugar-beet.—The results obtained in 1889 with Vilmorin's seed, bought directly, were superior to those obtained with the same variety of seed saved three generations running at Grignon; contrary to the experience of the previous years—the respective mean yields were 40,100 and 37,800 kilos. per hectare. Moreover, the superiority extended to the density of juice and percentage of sugar. The crops obtained with farmyard manure plus nitrate of soda were much larger than when it was omitted, and especially it was proved that at Grignon much better crops of sugar-beet are obtained when the farmyard manure is ploughed in in the autumn instead of spring.

Wheat.—The square-head wheat, which usually resists well, was laid in 1889 at Grignon; above all in the plots dressed with farmyard manure, and on strong soils it is recommended not to use this manure the same year, but at Grignon it may be, as a rule advisable.

Forage Maize.—The highest crop reached 59,700 kilos. per hectare, whereas in previous years 70,000—80,000 have been obtained. Even on plots highly manured for years previously the maize did not this year profit by the accumulation of organic matter in the soil, the great dryness of the summer probably accounting for this.

Oats.—The variety "avoine des salines," taken after sugar-beet, produced an average crop of 31·8 metric quintals per hectare; the variety "avoine géante à grappes" (giant cluster oat), 23·2 metric

quintals. On lea ground, the yields were 19·1 and 13·9 metric quintals respectively. J. M. H. M.

Chemistry of the Truffle. By A. CHATIN (*Compt. rend.*, **110**, 435—440; compare this vol., p. 659).—Truffles grown in soil containing 46·09 of calcium oxide contained 75 per cent. of water and 25 per cent. of solid matter, the latter consisting of nitrogen 2·08 parts, non-nitrogenous organic matter 20·42 parts, and ash 2·50 parts. The ash contained only 7·5 per cent. of calcium oxide.

Truffles grown in a highly ferruginous soil contained 74·9 per cent. of water and 25·1 per cent. of solid matter, composed of 4·10 parts of nitrogen, 2·80 parts of ash, and 18·20 parts of non-nitrogenous organic matter. The proportion of iron in the ash was normal; but although the soil contained only traces of phosphorus, the ash contained 23·15 per cent. of phosphoric anhydride.

The ash of the truffle contains about 25 per cent. of phosphoric anhydride, 7 to 8 per cent. of calcium oxide, and 5 per cent. of ferric oxide, and these proportions are not materially altered by variations in the composition of the soil. Manganese is always present in minute quantity, and iodine and chlorine are also constant constituents.

The truffle forms a complete food, rich in nitrogen and in the organic compounds essential to animal life. The proportion of nitrogen is independent of the quantity of nitrogen in the soil. C. H. B.

Absorption of Ammonia from the Air by Vegetable Soils. By T. SCHLOESING (*Compt. rend.*, **110**, 429—434, 499—504).—The soils were exposed in a gallery, through which was drawn air previously filtered through cloth. In order to determine the relation between the quantity of ammonia brought in contact with the soil under these conditions and the quantity which would have come in contact with it if it had been simply exposed to the air similar vessels containing sulphuric acid were exposed in the gallery, and to the open air. It was found that the quantities of ammonia absorbed were as 324 : 200, and hence it was necessary to make a correction for the difference.

Six non-calcareous soils, which had no power of absorbing free nitrogen, were exposed for 16 months, and during the summer were occasionally watered. In five cases there was a slight loss of ammoniacal nitrogen, but in five cases there was a decided gain in nitric nitrogen, amounting to from 26·7 to 38·0 kilos. per hectare per annum. In one of the experiments the gain was much greater even than this. The results, when corrected for the ammonia contained in the suspended matter of the air, and for the difference of conditions, gave an absorption of 15·3, 23·6, 50·1, 22·4, and 20·5 kilos. respectively per hectare per annum.

A soil containing 37 per cent. of calcium carbonate, a non-calcareous soil, and a subsoil gave respectively an increase of 90·1, 75·4, and 66·4 kilos. per hectare per annum, and these numbers, when corrected (200/374), become 47·1, 39·2, and 34·4 respectively.

Eight calcareous soils, containing from 2·1 to 11·15 per cent. of

calcium carbonate, all showed a slight increase in the amount of ammonia, and the increase in nitric nitrogen varied from 30·8 to 46·5 kilos. per hectare per annum (corr.).

The same soils exposed in a dry condition, fresh surfaces being exposed by raking up from time to time, absorbed about 0·130 gram of ammonia per kilo., but the increase in nitric nitrogen was very slight.

The absorption of ammonia is greatest when the difference between the tension of the ammonia in the soil and that in the atmosphere is at a maximum, and is, therefore, greatest when the soil is moist and when nitrification converts the ammonia into nitrates as fast as it is absorbed. When the earth is dry, nitrification is suspended, and the ammonia accumulates up to a certain point, beyond which the rate of absorption gradually diminishes. C. H. B.

Vegetable Soils and Atmospheric Ammonia. By BERTHELOT (*Compt. rend.*, **110**, 558—560).—Vegetable soils usually evolve ammonia, but under certain conditions can absorb this gas from the atmosphere. The conditions under which the interactions become reversed are extremely complex, and cannot be regulated or defined. Corrections based on the amount of ammonia absorbed by a given superficial area of dilute sulphuric acid are not admissible, because the action of the acid is not reversible, and does not resemble that of the soil. A coefficient deduced from experiments of this kind is not generally applicable, because the absorption taking place in one locality may be more than counterbalanced by evolution which is going ou at the same time in surrounding areas. Almost all investigators in this direction agree that the part played by atmospheric ammonia in the absorption of terrestrial nitrogen by plants is very small, and that vegetable soils are one of the chief sources from which the atmospheric ammonia is derived. C. H. B.

Remarks on the Observations of Berthelot on the Reactions between Vegetable Soil and Atmospheric Ammonia. By T. SCHLOESING (*Compt. rend.*, **110**, 612—613).—Purely polemical.

Composition of the Sea Mud in the New Alluvia of the Zuiderzee. By J. M. VAN BEMMELEN (*Landw. Versuchs-Stat.*, **37**, 239—256).—Analyses were made of the following soils:—(I.) The heavy clay from the former bay Y, which has been dammed in and cultivated. II. A lighter sea-clay, taken from the Zuiderzee, between Medemblik and the Island of Wieringen. III. Various samples of clay from the Zuiderzee. The following numbers show the percentages in I and II, in the soils dried over sulphuric acid:—

	CaO.	MgO.	K_2O.	Na_2O.	Fe_2O_3.	Al_2O_3.	SiO_2.	P_2O_5.
I.	5·73	2·26	2·59	1·13	5·64	14·10	52·5	0·17
II.	8·19	1·42	1·76	1·20	3·33	8·02	65·0	0·11

	CO_2.	Cl.	SO_3.	S.	Humus.	Water.
I.	—	—	—	—	6·93	4·85
II.	5·34	0·45	0·40	0·79	3·25	2·0

The amounts soluble in water, acetic, hydrochloric, sulphuric, and hydrofluoric acids, were determined, and are shown in tables.

The various other samples analysed were from newly-deposited clay and sand layers. The amount of sand they contained varied from 25 to over 90 per cent., whilst the percentage of calcium carbonate varied from 20 to 5. N. H. M.

Composition of the Volcanic Soils of Deli and Malang, and the Clay Soil of Rembang. By J. M. VAN BEMMELEN (*Landw. Versuchs-Stat.*, **37**, 257—278).—For the last 20 years tobacco culture in Deli (Sumatra) has continually developed, and an excellent produce is obtained. Samples of the soil, which is very fertile, were analysed, and the results compared with those obtained from the soil of Malang (Java) and that of Rembang, in Java, which formerly yielded excellent tobacco, but later gave a produce of bad quality. The results of analyses of two Deli soils are given, (I) a reddish-brown clay or loam, and (II) a gray soil, from near Medan. The volcanic clay from Malang (III and IV) is quite different from ordinary clay; the weathered portion is yellowish-brown and plastic. The alluvial clay of Rembang (V) is brownish-yellow, and contains varying amounts of sand. The following are the analytical results given in percentages of the soils dried over sulphuric acid:—

	I.	II.	III.	IV.	V.
CaO......	0·78	0·81	3·55	3·77	1·19
MgO	0·48	0·39	1·70	2·01	0·83
MnO.....	0·38	0·47	—	—	—
K_2O......	0·44	0·23	0·88	0·24	1·27
Na_2O.....	0·22	0·57	1·13	0·50	0·65
Fe_2O_3	7·03	4·85	9·05	7·35	5·12
Al_2O_3	26·59	12·82	25·20	11·40	12·87
SiO_2	26·19	20·92	44·74	67·5	60·66
Cl	0·02	trace	0·01	0·02	trace
SO_3......	0·06	0·03	small amount	small amount	0·06
S........	0·02	0·01	—	—	—
OH_2......	12·47	6·30	6·35	3·36	4·80
Humus ...	5·07	3·23	3·82	3·42	2·65
Minerals..	20·47	48·54	3·16	—	—
P_2O_5	0·19	0·12	0·20	0·19	0·13

N. H. M.

Analytical Chemistry.

New Gas Balance. By F. LUX (*Zeit. anal. Chem.*, **29**, 13—18). —The apparatus is identical in principle with the original pattern (*Zeit. anal. Chem.*, **26**, 38, *et seq.*), the gas stream being passed continuously through a globe attached to one arm of a balance, which, by its angle of deviation from the horizontal position indicates the weight,

and, therefore, density of the gas. The improvements now introduced consist of the use of an agate plane and steel knife-edge for the central support, a cylindrical arrestment, by which the beam can be held stationary in any position, and a rider by which the deviation from the horizontal can be reduced. M. J. S.

Volumetric Estimation of Bromine in the Presence of Chlorine and Iodine. By N. McCulloch (*Chem. News*, **60**, 259—260).—The proposed method is only applicable in the absence of oxidising and reducing agents and of metals forming bromides insoluble in dilute hydrochloric acid. It is an outcome of the method of titrating a hydrochloric acid solution of iodine or an iodide with standard permanganate until the free iodine is converted into colourless monochloride as indicated by means of chloroform (Abstr., 1888, 626), a method which in the present instance is applied to bromine and bromides to obtain a first approximate estimate of the amount present. The reactions involved in the new method are—1. The production of manganic chloride without the evolution of chlorine, by the action of hydrochloric acid on permanganate in the presence of manganous chloride, and the manganic chloride not being attacked by hydrocyanic acid. 2. The conversion of bromine or iodine or their hydracids into monochlorides by the manganic chloride. 3. The decomposition by hydrocyanic acid of the compounds of chlorine, bromine, and iodine with one another, the result being that when permanganate is added in excess to a solution of hydrocyanic and hydriodic acid containing the required proportions of manganous chloride, hydrochloric acid, and hydrocyanic acid, cyanogen chloride, bromide, and iodide are ultimately produced at the expense of the manganic chloride first formed; consequently the amount of this salt reduced is a measure of the quantity of bromine or iodine present, and is ascertained by estimating by the iodine method the nonreduced manganic chloride remaining in the solution. Under the prevailing conditions, the accuracy of the method is affected neither by the action of hydriodic acid on cyanogen bromide or iodide, nor by the spontaneous decomposition of the manganic chloride. The solutions required are permanganate (31·9 grains to 10,000 grains of water), potassium iodide (82·78 grains to 10,000 grains of water), chloroform, hydrocyanic acid (potassium cyanide solution, 600 grains of 95 per cent. salt to $13\frac{1}{2}$ ounces of water, acidified), and manganous chloride solution ($\frac{1}{2}$ lb. of crystallised salt to 4 ounces of water) containing 4 mols. of hydrochloric acid to every 3 mols. of the salt. All these reagents are purified to suit the requirements of the method, and whenever necessary are standardised under conditions similar to those to be encountered in their application. To make the estimation, the weighed bromide dissolved in $\frac{1}{2}$ ounce of water is treated with excess of the standard permanganate (the quantity required having been approximately determined by the method already alluded to) and cooled to 55° F. The manganic hydrate is dissolved by adding about one-third of the volume of the solution of strong hydrochloric acid; excess of hydrocyanic acid is then added and the whole cooled. After half an hour the solution is titrated with

standard iodide until nearly decolorised, and finally the excess of iodine is accurately determined by adding chloroform and titrating with permanganate. The bromine is calculated by taking the difference between the amounts of bromine represented by total permanganate and iodine used. If iodine is also present, it would be included in this bromine, and must therefore be determined separately by the permanganate-hydrochloric method and allowed for.

D. A. L.

Estimation of Free Halogens and of Iodides in Presence of Chlorides and Bromides. By P. LEBEAU (*Compt. rend.*, **110**, 520—522).—30 to 40 c.c. of carbon bisulphide and an equal volume of water is introduced into a flask holding about 200 c.c., and is mixed with a definite volume of the liquid to be analysed and a few drops of indigo sulphate solution. Standard bromine-water is then added drop by drop with vigorous agitation. The liberated iodine dissolves in the carbon bisulphide, and the upper layer of liquid remains blue until the whole of the iodine has been liberated. The slightest excess of bromine decolorises the indigo. The bromine solution must be kept in a bottle with a glass stopper, and used from a burette with a glass stop-cock, and its strength must be determined frequently.

Free halogens are best estimated by adding to the solution an excess of zinc powder and titrating the filtered liquid with standard silver nitrate.

C. H. B.

Volumetric Estimation of Sulphuric Acid. By A. GAWALOWSKI (*Zeit. anal. Chem.*, **29**, 19).—The author reaffirms the accuracy of his method (Abstr., 1888, 751), which had been disputed.

M. J. S.

Detection of Thiosulphuric Acid in Urine. By W. PRESCH (*Arch. path. Anat.*, **119**, 148—167).—See this vol., p. 812.

Estimation of Phosphoric Acid in the Presence of Silica. By K. PREIS (*Listy Chem.*, **13**, 153—154).—The author proves by numerous experiments that phosphoric acid may be estimated in the presence of pretty large quantities of silica (solution of soluble glass acidified with hydrochloric acid was employed), when the precipitate of ammonium phosphomolybdate is washed with pure, cold water. But as the liquid comes turbid through the filter towards the end, double filters should be used.

B. B.

Estimation of Total Phosphorus in Urine. By CHAPPELLE (*J. Pharm.* [5], **21**, 344—345).—10 c.c. of the urine is heated with 5 c.c. of sulphuric acid during several hours, or until the liquid becomes decolorised. The solution is diluted to 50 c.c., neutralised with sodium hydroxide, and precipitated with magnesium mixture in the usual way.

J. T.

Behaviour of Silica and its Compounds in Fused Microcosmic Salt. By J. HIRSCHWALD (*J. pr. Chem.* [2], **41**, 360—367).—

The insolubility of silica in fused microcosmic salt has long been recognised as a test for that substance.

If microcosmic salt is fused on a platinum loop and heated to the highest temperature of the blowpipe flame for some time, it gradually becomes turbid from the presence of crystals which, as seen magnified 400 times, are hexagonal pyramids; they are probably a sodium pyroborate, and evidently identical with the crystals obtained by Wunder (*J. pr. Chem.* [2], **1**, 460). The possibility of mistaking these crystals for undissolved silica is obvious.

A bead of fused sodium hexametaphosphate dissolved at a bright red heat 2·55 per cent. (of its original weight) of powdered rock crystal before it became turbid; but this number is probably lower than it should be, for phosphoric acid is most likely lost during the heating. No pyrophosphate crystals could be detected in the bead, but transparent, spindle-shaped crystals were seen after it had cooled.

Many mineral silicates, even in the form of splinters, dissolve completely in the fused salt. A classification of such silicates is given according as they dissolve in the form of powder to a clear glass (1) after some time, (2) easily, (3) very easily. The experiments were made with the aid of the microscope.

Many minerals free from silica remain undissolved in the fused salt. A. G. B.

Detecting Metallic Silver in the Presence of Lead. By A. Johnstone (*Chem. News*, **60**, 309).—The metallic bead obtained with fusion mixture on charcoal before the blowpipe, is dissolved in nitric acid, the solution nearly neutralised with sodium carbonate, and strips of copper and zinc immersed in it. The silver is deposited on the copper and can be tested, whilst the lead separates on the zinc. T. P. Blunt points out in a letter (*Chem. News*, **61**, 11) that a more rapid method of detecting silver is by adding a saturated solution of lead chloride to the solution containing the metallic bead dissolved in nitric acid. D. A. L.

Impurities in Commercial Barium Carbonate. By R. Wegscheider (*Zeit. anal. Chem.*, **29**, 20).—In a specimen from a well-known German maker, traces of zinc and iron were found. In another preparation, a not inconsiderable quantity of manganese was present. M. J. S.

Separation of Barium and Strontium. By R. Fresenius (*Zeit. anal. Chem.*, **29**, 20—28).—The author's experiments fully confirm the statement of Schweitzer that the action of cold ammonium carbonate, or that of boiling potassium carbonate mixed with sulphate, on a mixture of barium and strontium sulphates is totally different from their action on the individual sulphates when separate. However varied the mode of treatment, part of the barium sulphate was converted into carbonate, whilst part of the strontium sulphate remained unattacked, the proportions varying according to the preponderance of one or the other sulphate. Rose's methods of separation are therefore quite valueless. M. J. S.

Estimation of Zinc in Blende containing Manganese. By W. STAHL (*Chem. Centr.*, 1890, i, 297; from *Berg. Hutt. Zeit.*, **49**, 5—6).—The solution of blende in nitric acid is concentrated, and potassium chlorate is added as long as the green vapours of chlorous anhydride are evolved; the manganese being thus peroxidised. The mixture is boiled, diluted carefully with water, rendered ammoniacal, and filtered. The manganese and the greater portion of the lead are thus separated, and the remainder of the latter may be precipitated by ammonium phosphate. This precipitate must be dissolved in nitric acid, and reprecipitated in order to obtain all the zinc in solution, after which its quantity is determined by means of a standard solution of sodium hydrosulphide. J. W. L.

Sensitive Test for Certain Impurities in Mercury. By G. GORE (*Chem. News*, **61**, 40—41).—Pure mercury was treated with minute but known quantities of amalgams prepared from the same mercury, and the effect of these mixtures on electrolytes was observed by means of an ordinary astatic torsion galvanometer of 100 ohms resistance, 0·00013258 volt being the minimum degree of E.M.F. required to visibly move the needles. The results were as follows, the numbers being parts of mercury to one of the foreign metal:—

Metal added.	Electrolyte consisting of	
	1 grain HCl or H_2SO_4 in 120 c.c. water.	10 grains KCl in 120 c.c. water.
Magnesium	110,274,000,000	13,430,858,806
Zinc	104,950,000,000	18,034,482,758
Cadmium	184,828,432	10,404,225
Tin	38,900,000	8,831,632
Copper	15,484,375	1,640,160
Bismuth	9,762,300	1,621,000
Lead	5,651,149	1,050,341
Silver	905	79

This forms a delicate means of detecting impurities of this class in mercury; some mercury containing all the above metals was found to produce no deflection of the needle after a second distillation.

D. A. L.

Volumetric Estimation of Iron in Ferrum Reductum. By A. PARTHEIL (*Chem. Centr.*, 1890, i, 495—496; from *Apoth. Zeit.*, **5**, 55).—The author has applied the following method to the estimation of the iron in ferrum reductum, on the supposition that it consists of a mixture of metallic iron and magnetic oxide of iron, and the results are satisfactory.

1 gram ferrum reductum is dissolved in a 200 c.c. flask with 40—50 c.c. of sulphuric acid (1 : 5). Potassium permanganate solution is now added drop by drop until the solution is just coloured, any slight excess being reduced by the addition of a minute quantity

of sugar. The solution is now diluted to the mark, and 50 c.c. (=0·25 gram ferrum reductum) added to a solution of 2 grams of potassium iodide, and finally a few c.c. of hydrochloric acid. After remaining an hour at the ordinary temperature, the free iodine is estimated by titration with decinormal sodium thiosulphate, starch being used as indicator. Ferrum pulv. is treated in the same way. The total percentage of iron is obtained from the number of c.c. of sodium thiosulphate used, and that of metallic iron is obtained by the use of the formula :—

$$Z = \frac{2·03\,m}{p} - 262·5,$$

where p = weight of substance in grams, m = c.c. sodium thio sulphate. J. W. L.

Analysis of Chrome-Iron Ore. By R. FRESENIUS and E. HINTZ (*Zeit. anal. Chem.*, **29**, 28—35).—The following method was adopted with success for a very refractory ore containing 61 per cent. of chromium, 28 per cent. of iron, and 9 per cent. of combined carbon and graphite. About 5 grams of the mineral, placed in a porcelain boat, is gradually heated in a stream of dry chlorine, in a hard-glass tube, connected with a Péligot's tube, a Woulff's bottle, and two more Péligot's tubes in succession, all of which contain water. The heat is so regulated that most of the ferric chloride condenses in the tube. When cold, the receivers are exchanged for a fresh Péligot tube containing water, the chlorine is displaced by carbonic anhydride, and then dry hydrogen passed through, while the boat and the sublimate are gently heated, to reduce part of the chromic chloride to chromous chloride, and thus render it soluble. After cooling, the contents of the boat, consisting of carbonaceous matter, graphite, slag, particles of unattacked chrome ore, manganous chloride, and traces of iron and chromium chlorides, are washed, dried, and ignited in a stream of oxygen, then in hydrogen to reduce the oxide of iron, and then again in chlorine with the original receivers. Any residue now remaining is washed, dried, and weighed, and if its amount is considerable is further analysed. The second sublimate is heated in hydrogen like the first, and the contents of the two tubes are then treated with a measured quantity of hydrochloric acid of sp. gr. 1·1, and the solution added to the contents of the receivers, and the washings of the residue in the boat. If this liquid does not remain clear, the sediment is collected, and fused with a mixture of sodium carbonate and potassium chlorate, and the solution of the fused mass is evaporated with hydrochloric acid to dryness, and again taken up with a known volume of hydrochloric acid of 1·1 sp. gr. Any insoluble matter is washed, dried, and preserved; the solution is added to the principal one. A sufficient amount of sodium carbonate is now added to leave about 4 per cent. of hydrochloric acid (of 1·1 sp. gr.) free, and the liquid is then treated with hydrogen sulphide, first at 70°, and then cold. The precipitate is dissolved in hydrochloric acid containing bromine, and the solution, after removal of the bromine by ammonia, is again acidified with hydrochloric acid, and

precipitated by hydrogen sulphide. The metals of the 5th and 6th groups contained in this precipitate are separated by the usual methods. The filtrate is added to the principal one, which is then evaporated to dryness for the separation of the silica, and the precipitate is ignited together with that obtained from the fusion. If white, it is weighed; the silica is removed by heating with hydrofluoric acid; any residue is fused with potassium hydrogen sulphate, and tested for titanic acid by boiling, and for bases by ammonia. If it is not white, it must be fused with sodium carbonate and potassium nitrate, and the solution again evaporated with hydrochloric acid, the filtrate being then united with the principal solution, and the precipitate treated as above.

The solution is now treated with chlorine, the excess of which is expelled by heating. After evaporating to about a litre, and cooling, it is nearly neutralised with sodium carbonate, and mixed in a flask with a small excess of precipitated barium carbonate. The precipitate is thoroughly washed, dissolved in hydrochloric acid, and made up accurately to 1 litre. Of this, 200 c.c. is evaporated, and the barium it contains is precipitated by cautious addition of sulphuric acid to the hot solution, avoiding excess. The filtrates from the barium sulphate (which requires to be repeatedly digested with hydrochloric acid to free it from iron and chromium) are evaporated, mixed with sodium carbonate and potassium chlorate, and fused. The melt is extracted with hot water, and the residue fused a second time with carbonate and chlorate. The ferric oxide is finally dissolved in hydrochloric acid, and precipitated with ammonia as usual. It should be tested for alumina and silica, and these, if necessary, deducted. The solution containing the chromium is made alkaline with ammonia. Any precipitate produced is collected on a filter and examined for alumina, aluminium phosphate, silica, and titanic acid. The chromate is finally reduced by hydrochloric acid and alcohol, and precipitated as chromic oxide. This precipitate may contain phosphoric acid.

The filtrate from the barium carbonate precipitate will contain the manganese, nickel, cobalt, and zinc. It is freed from barium as above, and after nearly neutralising with ammonia, is mixed with ammonium acetate, and treated with hydrogen sulphide, which throws down nickel, cobalt, and zinc. These are separated by the usual methods, whilst the manganese in the filtrate is precipitated first with bromine and ammonia, and then, for removal of alkali, with ammonium sulphide.

For the estimation of the carbon, phosphorus, and sulphur, 5 grams is treated with chlorine as above, and the contents of the boat are digested with a mixture of chromous chloride and hydrochloric acid, and filtered through an asbestos filter. The carbon is thoroughly washed, and then oxidised by chromic and sulphuric acids. The solution in the receivers, which contains all the sulphur and phosphorus as sulphuric and phosphoric acids, is evaporated with addition of sodium chloride for removal of silica; the sulphuric acid is precipitated by barium chloride, and the phosphoric acid from the filtrate (after evaporation with nitric acid for removal of chlorides)

by molybdate, with the usual precautions. Any arsenic in the mineral will accompany the phosphoric acid, and after weighing the magnesium phosphate it must be precipitated as sulphide and deducted.

For estimating the graphite, 10 grams of the very finely-powdered ore is digested with hydrochloric acid until the residue is no longer affected by a magnet brought near the flask. This requires some weeks. The graphitic residue is washed on an asbestos filter with water, potash, alcohol, and ether, and its amount ascertained by oxidation with chromic and sulphuric acids. M. J. S.

Detection of Tin in Minerals. By A. JOHNSTONE (*Chem. News*, **60**, 271).—The mineral is heated before the blowpipe on charcoal with white flux, sometimes with the addition of borax or potassium cyanide or both. The ignited residue with some of the surrounding carbon is crushed in a mortar, washed with water, and the metallic scales remaining behind tested for tin, by dissolving in hydrochloric acid, and treating with gold chloride or with hydrogen sulphide.

D. A. L.

Quantitative Estimation of Antimony. By F. BEILSTEIN and O. v. BLAESE (*Chem. Centr.*, 1890, i, 350; from *Bull. Acad. St. Pétersbourg* [2], 1, 209—211).—The authors recommended that antimony should be weighed as sodium antimonate, $NaSbO_3 + 3\frac{1}{2}H_2O$. Of the air-dried salt, 1000 parts of water at 12·3° dissolves 0·31 part; 1000 parts of alcohol of 15·8 per cent. at 12·3° dissolves 0·13 part; 1000 parts of alcohol of 25·6 per cent. at 12·3° dissolves 0·07 part; of the freshly precipitated and washed salt, 1000 parts of alcohol of 25·5 per cent. at 18·1° dissolves 0·0956 part. Sodium hydroxide and carbonate reduce the solubility of the salt somewhat; ammonia and potassium salt dissolve the salt rather more than water; in glacial acetic acid the salt is quite insoluble.

The authors, therefore, recommend the following method:—The precipitated antimony sulphide is washed from the filter with water, and warmed with addition of concentrated sodium hydroxide solution and 70 c.c. of hydrogen peroxide. After the oxygen has been evolved, one-third of the volume of 90 per cent. alcohol is added, and the whole allowed to remain for 36 hours in the cold. The precipitated sodium antimonate is first washed by decantation, then on the filter, with a solution consisting of 1000 c.c. of 25 per cent. alcohol, 7 grams of sodium acetate, and 7 c.c. of glacial acetic acid, until no trace of sulphuric acid remains; then, finally, with 50 per cent. alcohol. The analyses are very satisfactory. J. W. L.

Estimating Minute Quantities of Gold. By G. TATE (*Chem. News*, **61**, 43—46; 54—55; 67—70).—The author advocates and fully describes the microscopic measurement of beads of gold obtained in assays, and its application to the estimation of that metal. Beads as small as 0·00075 inch diameter, and representing 0·000001 grain, can be measured; the method is, therefore, susceptible of great accuracy, and requires smaller quantities for analysis than gravimetric methods.

Various experimental results show:—1. The even distribution of gold in ingots of lead-gold alloy; 2. That the loss of gold in parting gold-silver alloy increases with the proportion of the latter metal; 3. That in cupellation there is practically no loss of gold; and 4. That very minute quantities of gold can be separated from highly complex mixtures, and detected by the use of the microscopic method.

D. A. L.

Electrolytic Estimation of Palladium. By E. F. SMITH and H. F. KELLER (*Amer. Chem. J.*, **12**, 212—216).—Attempts to electrolyse a solution of palladium cyanide with excess of potassium cyanide, or of palladious chloride with a large excess of potassium thiocyanate, did not give quantitative results; the deposited metal was black, and exhibited spongy spots. Good results were obtained by electrolysing a solution made by dissolving 0·2228 gram of palladio-diammonium chloride, $PdN_2H_6Cl_2$, in ammonia, and adding 20 to 30 c.c. of the same reagent (sp. gr. 0·935) and 75 c.c. of water. The current was of such a strength as to generate 0·9 c.c. of mixed gases per minute in a water voltameter, and was allowed to run during the night. Good results were also obtained with a slightly larger excess of ammonia, and a current giving 0·8 c.c. per minute, running for 16 hours, and also with double the amount of palladium, and a current giving 0·7 c.c. per minute running for 18 hours. It was necessary to have excess of ammonia present in order to prevent the deposition of palladium oxide on the positive pole. The deposit of palladium, which was bright and metallic in appearance, was dried at 110° to 115°. As it was very slow in dissolving, even in fuming nitric acid, it was found expedient to first coat the platinum vessels employed with a thin layer of silver.

C. F. B.

Colorimetric Methods for Determining Nitrates in Potable Waters. By S. RIDEAL (*Chem. News*, **60**, 261).—The "phenol sulphuric acid" and "carbazole" tests are compared. In the "phenol sulphuric acid" experiments, a solution containing 0·7215 gram of potassium nitrate per litre, and "phenol sulphuric acid," prepared by dissolving 15 grams of phenol in 92·5 c.c. of sulphuric acid, diluted with 7·5 c.c. of water, were employed; 1 c.c. of the latter was applied to the dry residue from the water, to which was then added 1 c.c. of water and 3 drops of sulphuric acid; the whole being now gently warmed, diluted, transferred to a Nessler tube made up to 100 c.c., and the colour compared with that obtained with the standard nitrate. In the carbazole tests, 100 c.c. of water was taken, the chlorine precipitated with silver sulphate (4·3945 grams per litre), 2 c.c. of aluminium sulphate (5 grams per litre) added, the whole made up to suitable bulk, and filtered. To 2 c.c. of the filtrate, 4 c.c. of sulphuric acid was added, and when cool, 1 c.c. of a mixture, prepared by mixing 1 c.c. of glacial acetic acid solution of carbazole (containing 0·6 gram per 100 c.c.) with 15 c.c. of sulphuric acid, the colour being compared against the standard nitrate. The results from five different waters were:—

	Nitrogen in parts per 100,000.				
	1.	2.	3.	4.	5.
By "phenol sulphuric acid"	0·025	0·050	0·200	1·400	1·60
By carbazole	0·025	0·045	0·209	1·380	1·65

D. A. L.

Colorimetric Methods for Determining Nitrates in Potable Waters. By A. E. JOHNSON (*Chem. News*, **61**, 15).—Referring to the note by S. Rideal (preceding abstract) on this subject, the author points out that he prefers using a standard nitrate solution of one-tenth the strength—100 c.c. of the 0·7215 gram solution, diluted to a litre; moreover, he prepares his "phenol sulphuric acid" by digesting the mixture for eight hours in a boiling water bath, and, when cool, adding water and hydrochloric acid; convenient quantities are 80 c.c. of liquefied crystalline phenol, 200 c.c. of H_2SO_4, and 420 c.c. of H_2O, and 140 c.c. of HCl. His procedure is, briefly:—The water and standard nitrate are evaporated to dryness simultaneously, and the residue in each case is treated with 1 c.c. of the "phenol sulphuric acid," and heated gently for 15 minutes; with bad waters, a red colour soon appears; then they are diluted, treated with ammonia, and the colour compared in Nessler tubes, &c. Larger quantities of water and less nitrate are evaporated for good waters, whilst bad waters may even be diluted. D. A. L.

Estimation of Water, Humus, Sulphur, &c., in Soils. By J. M. VAN BEMMELEN (*Landw. Versuchs.-Stat.*, **37**, 279—290).—With regard to the estimation of water, the colloïdal substances present in soils retain more or less water. according to (1) their composition and state of equilibrium, (2) the tension of the aqueous vapour, and (3) the temperature. The amount of water lost by an air-dried soil at 100°, has no special meaning, and it is suggested that, for comparison, the results of analyses should be calculated to show percentages in the soils dried over sulphuric acid. The water which remains, the strongly combined water, is determined separately. The humus is determined by multiplying the amount of carbon by 1·724. The amount of carbon is found, in the case of soils containing calcium carbonate, by adding the amount which remains as carbonate after burning, to that absorbed as carbonic anhydride in the potash bulbs, and deducting that of the carbonates originally present, which is separately determined.

The carbonates are determined at the ordinary temperature; if the soil is boiled with acid, too high results will be obtained, owing to the partial decomposition of the humus.

The loss by ignition can only be considered as the snm of the humus and water, in the case of soils which contain no carbonates, chlorides, and sulphides. Moistening the ignited soil with ammonium carbonate solution is to be avoided for several reasons. In the case of sea-mud, the author determined the carbonic anhydride, sulphuric acid, and chlorine in the soil before and after ignition, and then applied the necessary correction.

The strongly combined water cannot be determined exactly, and is

derived either from the difference between loss on ignition and the humus, or from the difference between the amount of water determined by analysis and the amount of water corresponding with the humus. In volcanic soils, the humus was assumed to contain 5 per cent., and in soils derived from the sea 6 per cent. of water.

In the estimation of sulphuric acid, difficulties may arise from the insolubility of a small part of the sulphates, and from the presence of sulphur in the organic matter of the soil. If the aqueous extract contains ferric oxide or more than a trace of humus, these must be got rid of, or the results will not be exact. In the analysis of soils which gave extracts containing only a little humus, the silicic acid was removed, then the ferric oxide and alumina were precipitated by boiling sodium carbonate, the solution acidified and precipitated with barium chloride and filtered after two days. The ferric oxide and alumina were redissolved, the solution treated with barium chloride, and kept for some days. Another method employed was to heat the substance with an excess of sodium carbonate in a stream of oxygen in a combustion-tube, the temperature being kept sufficiently low to prevent the glass from being attacked. Sulphuric acid was also determined by heating the substance with sodium carbonate and potassium nitrate in a platinum crucible at a dull red heat. The solutions were always evaporated on the water-bath, and not directly over a gas flame.

Silicic acid and alumina in the colloïdal silicates were determined in successive extracts, made with dilute hydrochloric acid, dilute potash, stronger hydrochloric acid, dilute potash. The residues of the solutions are heated with sulphuric acid to destroy the organic matter. The silica is then completely, or almost completely, separated from the alumina, when the residue is treated with hydrochloric acid. The silica is always tested with hydrofluoric acid to see if it is pure. In estimations of alumina and silica, the latter, after it has been weighed, is treated with hydrofluoric and sulphuric acids, and the small amount of alumina in the residue determined.

The alkaline bases are separated from the alkaline earths by Deville's method, with oxalic acid, after precipitating any sulphuric acid which may be present. Corrections are applied for a trace of lime and potash in the oxalic acid, and for the small amount of magnesia which remains with the alkalis.

Manganese is most conveniently determined by Carnot's method (Abstr., 1889, 443). The hydrochloric acid extract of the soil is evaporated down, heated with potassium hydrogen sulphate, and the neutralised solution of the residue precipitated with hydrogen peroxide solution (20 c.c.), and ammonia (30 c.c.). The precipitate is washed by decantation, put into the carbonic acid apparatus, and treated with oxalic and dilute sulphuric acids. From the amount of carbonic anhydride obtained, the amount of manganese is calculated, assuming the precipitate to have the formula Mn_6O_{11} (Carnot, *loc. cit.*).

N. H. M.

Estimation of Ash in Food and Drugs. By W. KWASNIK (*Arch. Pharm.* [3], **28**, 178—182).—This operation is much facilitated by mixing the powdered substance with an equal weight of Kassner's

recently described calcium plumbate. In the case of liquids, such as milk, the residue, after evaporation, is charred, mixed with the plumbate, and roasted. Any plumbate reduced is re-oxidised, and the temperature is so low that chlorides are not volatilised. Results quoted to show the exactness of the process are perfectly satisfactory.

J. T.

Maumené's Test for Essential Oils. By R. WILLIAMS (*Chem. News*, **61**, 64—65).—The successful working of this test is influenced by the nature of the oil, the strength of acid used, by the mode of adding the acid, and manner of stirring. The author has applied it to many essential oils in the following manner:—100 fluid grains of oil was mixed with 20 fluid grains of sulphuric acid, in a beaker surrounded with cotton-wool, and stirred vigorously with a thermometer. The numerous figures obtained in this manner are tabulated, and indicate a probable useful application of the test, especially for confirming the presence of resin in oil of cassia. D. A. L.

Estimation of Ferrocyanides in the Bye-products of Gas Works. By R. GASCH (*Chem. Centr.*, 1890, i, 294—295; from *J. Gasbeleucht Wasserversorg*, **32**, 966).—Of the several methods which have been recently recommended for the determination of ferrocyanides in the bye-products of gas works, the author considers Zulkowsky's (Abstr., 1884, 501) the most applicable. He recommends, however, a solution of uranium acetate, 1 per cent., instead of ferric chloride, as indicator, a drop of the solution which is being titrated being brought on to a porcelain slab to which is added a drop of the uranium acetate solution, when the presence of any excess of ferrocyanide is indicated by the formation of a brown coloration. Moreover, instead of preparing a standard solution of potassium zinc sulphate, the author prefers the use of a standard solution of potassium ferrocyanide containing 20 grams per litre, with which the strength of the zinc solution may be readily determined. In applying the method to old gas-waste, 20 grams are rubbed in a warm mortar, with a little (15—20 per cent.) sodium hydroxide solution, and warm water gradually added until the whole is of a thin consistence; it is then filled into a 200 c.c. flask, shaken, and filtered directly into the burette from which the titration is made. In the case of gas liquor, it is desirable to add a crystal of ferrous sulphate and a small piece of sodium hydroxide. The formation of ferrous cyanide proceeds readily, and may be hastened by warming, after which the determination is carried out in the usual manner. If it is found that so little ferrocyanide is present that it cannot be directly determined, it is precipitated as Prussian blue, filtered, and dissolved in potassium hydroxide solution, which is then titrated from the burette as in the preceding case. J. W. L.

Volumetric Estimation of Potassium Ferricyanide. By G. KASSNER (*Arch. Pharm.* [3], **28**, 182—186).—A weighed quantity of ferricyanide is dissolved in water, and treated with so much potassium hydroxide that an excess remains after the reduction of the salt, and sufficient but not too much hydrogen peroxide is added, so that in a

few seconds the liquid takes a scarcely perceptible yellow tint. To remove the excess of peroxide, the alkaline liquid is heated to boiling, until a drop of the solution gives no coloration when added to potassium iodide and starch. The solution is then cooled considerably, diluted, acidified with dilute sulphuric acid, and titrated with potassium permanganate. The results are very exact. J. T.

Assay of Commercial Glycerol. By M. VIZERN (*J. Pharm.* [5], **21**, 345—347).—Crude glycerol is usually sold by soap-makers as containing 80 per cent. of glycerol. This is affirmed on the part of buyers to be indicated by a minimum sp. gr. of 1·300 at 15°, and a boiling point of 155°. The author shows that an imitation crude glycerol of 80 per cent. strength had a sp. gr. of 1·289 and boiling point of 136° at 756 mm. Commercial samples were titrated for glycerol with dichromate (Hehner's method) after treatment with silver oxide and basic lead acetate. The results show that it is impossible to determine exactly the amount of glycerol in a sample by the specific gravity and boiling point, also that 80 per cent. glycerol has generally a density below 1·3, and a boiling point below 150°. J. T.

The Value of the Phenylhydrazine Test for Sugar. By J. A. HIRSCHL (*Zeit. physiol. Chem.*, **14**, 377—389).—Many tests for sugar in urine are fallacious, because the reactions in question are given by other substances as well.

The most trustworthy tests are those with yeast, and with the polarimeter. Recently, v. Jaksch has introduced the phenylhydrazine test (Abstr., 1886, 744), and the present investigation is directed to determining whether this test may be added as a third trustworthy reaction for detecting the presence of sugar in urine. Such an investigation is all the more necessary since Thierfelder (Abstr., 1887, 717) and Geyer (*Wiener med. Presse*, **30**, 1686) have stated that glycuronic acid, a substance very liable to be mistaken for sugar, forms a compound with phenylhydrazine acetate analogous to that on the formation of which the detection of sugar depends. Geyer, indeed, states that the resemblance of the crystalline compounds obtainable is so close as to render the test of little value.

In the present research, experiments were first performed with pure sodium glycuronate. This was dissolved in water and mixed with phenylhydrazine hydrochloride and sodium acetate in the usual way, and placed in the water-bath at 100° for a quarter of an hour. It was then removed, and the precipitate which formed on cooling examined microscopically. The needles which were present mixed with amorphous matter were thicker than those of phenylglucosazone, but showed the same radial grouping, and were difficult to distinguish from them. If, however, the mixture was allowed to remain for a longer time than a quarter of an hour (30—60 minutes) in the water-bath, the precipitate obtained was amorphous, brownish-yellow, and altogether different and easily distinguishable from phenylglucosazone. Its melting point, after half-an-hour's stay in the water-bath, was 107—108°; after an hour, 150°. Fifty different kinds of urine

were then submitted to the test: an hour's stay in the water-bath was always employed; 45 of these gave the amorphous, brown precipitate with a melting point of 150°. In one case there was no precipitate. In four cases there was the typical formation of yellow, crystalline needles (melting point 205°). In these four cases alone the fermentation test gave positive results; three were from patients suffering from diabetes mellitus, the fourth was a case of glycosuria occurring in a patient with cerebral hæmorrhage.

If the amorphous precipitate obtained in the first 45 cases consisted of the phenylhydrazine-compound of glycuronic acid, it would appear that glycuronic acid is a constant constituent of human urine.

In addition to dextrose, three other sugars have been described in human urine: (1) levulose (Zimmer, *Deutsch. med. Woch.*, **2**, 329; Seegen, *Centr. med. Wiss.*, **22**, 753); this has been found only, mixed with dextrose, in diabetes. It cannot be distinguished from dextrose by the phenylhydrazine test, but only by the polarimeter. (2) Lactose (Hofmeister, *Zeit. physiol. Chem.*, **1**, 101). This is found only in the urine of suckling women. The compound, phenyllactosazone, formed by the action of phenylhydrazine, occurs in needles, which are about ten times the width of those of phenylglucosazone, and do not show the same orderly arrangement. Their melting point is 200°. (3) Maltose has been found in diabetic urine (Le Nobel); this gives a precipitate of phenylmaltosazone, which occurs in yellow tables melting at 82°.

The conclusions drawn are that the phenylhydrazine test is a perfectly trustworthy one.

(1) If the urine gives perfectly typical needles of phenylglucosazone, it certainly contains glucose. 0·03 per cent. of sugar in urine, 0·003 per cent. of sugar in water, can by this means be detected.

(2) It is essential that the test-tube should be allowed to remain one hour in the water-bath.

(3) If the result is a yellowish-brown, amorphous precipitate, sugar is not present, but the substance which behaves in this way is probably glycuronic acid. W. D. H.

Estimation of Sugar in Urine by Fermentation. By P. GUTTMANN (*Chem. Centr.*, 1890, i, 355—356; from *Deut. med. Wochenschr.*, **16**, 7—9).—The author has not found Einhorn's method, in which the carbonic anhydride obtained by fermentation is estimated, very suitable for the determination of sugar in diabetic urine. On the other hand, Roberts' method (*Med. Journ. Edinburgh*, 1861, 326) has given satisfactory results. 100—120 c.c. of the urine is filled into a vessel, and treated with 5—10 grams of fresh yeast, and then allowed to ferment. The density is determined before and after the fermentation at 15°, from which, by means of Worm-Müller's formula (*Pflüger's Archiv*, **33**, 211—220), the amount of sugar is obtained. J. W. L.

Estimation of Inverted Sugar. By J. FORMÁNEK (*Listy Chem.*, **14**, 132).—The solution precipitated with Fehling's solution is poured on to a filter containing water, in order to prevent it from

absorbing copper solution, which cannot subsequently be washed out, and the washed cuprous oxide is dissolved in nitric acid on the filter, washed out, and the copper estimated by electrolysis of the solution.

B. B.

Estimation of Acetone in Methyl Alcohol and in the Liquids used for Methylating Alcohol. By L. VIGNON (*Compt. rend.*, **110**, 534—536).—The acetone is converted into iodoform ($C_3H_6O = CHI_3$), which is extracted with ether free from alcohol, and weighed after evaporation of the ether. Krämer (Abstr., 1880, 826) specifies certain quantities of iodine and sodium hydroxide, but the quantity of iodine required for complete conversion of the acetone into iodoform varies with the order in which the liquids are mixed, and with other conditions of experiment, and if the iodine is not in large excess the results are too low. The author recommends the following mode of working. 5 c.c. of the liquid to be examined is diluted to 250 c.c. 5 c.c. of this mixture is agitated with 10 c.c. of binormal sodium hydroxide in a graduated and stoppered cylinder holding 100 c.c., and 5 c.c. of binormal iodine in potassium iodide is then added. After vigorous agitation, 10 c.c. of ether free from alcohol is added. The volume of the ethereal solution is observed, and 5 c.c. is withdrawn, evaporated in a vacuum, and the iodoform weighed. If V is the volume of the ethereal solution, p the weight of the iodoform, and x the weight of acetone in 100 c.c. of the liquid,

$$x = 1000\,pV\ 58/5 \times 394 = pV \times 29{\cdot}44.$$

The method is only applicable in absence of aldehyde, ethyl alcohol, or any substance besides acetone which will yield iodoform.

C. H. B.

Estimation of Acetone as Iodoform. By G. ARACHEQUESNE (*Compt. rend.*, **110**, 642—644).—Complete conversion of acetone into iodoform requires a quantity of iodine considerably in excess of the calculated quantity. In addition to sodium acetate and sodium iodide, iodate and formate, and probably salts of some other organic acids, are formed. Krämer recommends too low a proportion of iodine or too large a quantity of the liquid to be examined (compare preceding abstract). C. H. B.

Estimation of Fat in Milk. By LEZÉ (*Compt. rend.*, **110**, 647—649).—The process is based on the fact that if the milk is treated with an acid, and afterwards with ammonia, the fat separates readily.

A mixture of 100 vols. of milk with 200 to 250 vols. of pure concentrated hydrochloric acid is placed in a flask with a long graduated neck, heated until the liquid acquires a brown colour, and then mixed with dilute ammonia until the fat gradually separates, and the liquid becomes clear. Warm water is added so that the fat is brought into the graduated neck, and the volume of the fat is read off. The fat melts at 32—33°, and its sp. gr. at 15° is 0·93. At the melting point its sp. gr. is 0·90, and hence the volume of the fat in cubic centimetres × 0·9 gives the weight of fat in the quantity of milk taken. Good

results are obtained with 44 c.c. of milk and 100 c.c. of acid. The temperature at which separation occurs readily is about 80°.

C. H. B.

Analysis of Butter. By S. BONDZYŃSKI and H. RUFI (*Zeit. anal. Chem.*, **29**, 1—6).—The most characteristic constituents of butter are the volatile fatty acids, or rather their glycerides. Since the same acids are also freely soluble in water, the separation of them by distillation can be replaced by one of the following more convenient methods:—(1.) 4—5 grams of the butter is saponified with 50—60 c.c. of N/2 alcoholic potash, and the unneutralised potash is titrated by N/2 hydrochloric acid. The alcohol is then evaporated off, and the soap is decomposed by an excess of hydrochloric acid. The precipitated, insoluble fatty acids are washed with hot water on a filter, dissolved in alcohol, and titrated with N/2 or N/4 potash. The difference between the quantity of potash neutralised in the saponification and that required by the insoluble acids gives the amount corresponding with the volatile acids. (2.) 4—5 grams of the butter is saponified; the alcohol is removed by evaporation, and the aqueous solution is treated with the exact amount of hydrochloric acid necessary for neutralising the potash used. The insoluble fatty acids are washed, and the soluble acids in the filtrate are titrated with N/10 potash. The results of these methods agree with one another, and with the distillation process. The insoluble acids can be dissolved in ether, and weighed after evaporation. If then titrated with potash, the corresponding amount of glycerol can be calculated, and therefrom that of the glycerides of the insoluble acids, which by difference gives the amount of the glycerides of the volatile acids.

Fresh butter always contains small quantities of free insoluble acids and oleïc acid; free volatile acids are not present. As the butter becomes rancid, the increase in acidity is due mainly to the insoluble acids. Free volatile acids are only developed at a somewhat advanced stage of rancidity. The free acids can be estimated by dissolving about 20 grams of the butter in alcohol and ether, and titrating with N/20 alcoholic potash. Or an ethereal solution may be treated with dry calcium hydroxide, when the calcium salts of palmitic, stearic, and other related acids form a precipitate, which can be collected, decomposed by sulphuric acid, and extracted with ether. The calcium oleate remains in solution. If the solution is evaporated and burnt, and the lime weighed, the oleïc acid can be calculated from it. Free volatile acids can be estimated by melting the butter in hot water, washing on a filter, and titrating the filtrate. Phenolphthaleïn should in all cases be used as indicator.

Some experiments have also been made towards the estimation of hydroxy-acids in butter by Benedikt's acetylation method (Abstr., 1887, 620). The acetyl number 18·2 was found for butter.

M. J. S.

Valuation of Crude Cocaïne from Peru. By E. R. SQUIBB (*Zeit. anal. Chem.*, **28**, 743—744).—A moisture estimation is made in the usual way: 2 grams of the sample is then dissolved in 12 c.c. of ether (0·725 sp. gr.), and filtered from insoluble matter, which is washed with ether, dried, and weighed. The ethereal solution, which will

amount to about 50 c.c., is shaken with 10 c.c. of normal oxalic acid in a separation bulb. The acid is then run into a second separation bulb, and the ethereal solution is shaken with 10 c.c. of water containing 2 drops of oxalic acid, and then twice with 3 c.c. of water, these aqueous liquids being then added to the acid. The washed ethereal solution is now run into a tared beaker, the bulb is rinsed with 15 c.c. of ether and 2 c.c. of water, all of which is added to the acid solution. After subsiding, the acid layer is run back into the first bulb, and the ether, after twice washing with 3 c.c. of water, is added to the former ethereal solution, and the whole evaporated to obtain the weight of the impurities soluble in ether. The bulb is once more rinsed with 15 c.c. of ether and 2 c.c. of water, which mixture is added to the acid solution. This is then treated with normal soda, adding 1 drop in excess of neutrality. After shaking and settling, the sodium oxalate is run into the empty bulb, the ether is washed twice with 3 c.c. of water, and run into a tared beaker, taking care that no water accompanies it. The bulb is rinsed with 10 c.c. of ether and 2 c.c. of water. This is added to the oxalate solution with 1 drop more of soda. After vigorous shaking, the aqueous liquor is run away. The ethereal liquid is added to the previous one, and the whole evaporated. The cocaïne is dried at 90° and weighed. Recent estimations have given 94 per cent. in the best sorts, and 78 in the worst. M. J. S.

Cocaïne Chromate. By K. Mezger (*Chem. Centr.*, 1890, i, 352; from *Pharm. Zeit.*, **34**, 697—698).—From a hydrochloric acid solution, chromic acid precipitates the *cocaïne chromate*, $C_{17}H_{21}NO_4,H_2CrO_4$, in beautiful, silky, lustrous plates. If 0·05 gram of crystallised cocaïne hydrochloride is dissolved in 5 c.c. of water, and five drops of a 5 per cent. solution of chromic acid added, a distinct precipitate is formed as each drop falls into the solution; this, however, immediately dissolves again. If now 1 c.c. of strong hydrochloric acid is added, a heavy, yellow precipitate of the chromate is formed. Of the other alkaloïds, ecgonine, sparteïne, atropine, caffeïne, pilocarpine, codeïne, and morphine do not form yellow precipitates with chromic acid or potassium chromate, whereas quinine, quinidine, cinchonidine, cinchonine, hydroquinine, apomorphine, brucine, strychnine, and veratrine form precipitates with 5 per cent. chromic acid if the solutions are neutral, cocaïne being the only one which is precipitated only after the addition of hydrochloric acid. J. W. L.

Estimation of Paratoluidine. By G. A. Schoen (*Zeit. anal. Chem.*, **29**, 86; from *Bull. de Mulhouse*, 1888, 365).—A mixture of the hydrochlorides of para- and ortho-toluidine (which must be free from aniline and xylidine) gives with potassium dichromate a brown precipitate and a red filtrate. The intensity of the red coloration depends on the amount of paratoluidine present. The amount must first be learnt approximately from the specific gravity (that of paratoluidine is 0·99, of orthotoluidine, 1·004, at 15°), and if above 8 per cent., must be reduced by an appropriate addition of orthotoluidine. 1 c.c. of the mixture is then shaken with 2 c.c. of hydrochloric acid

and 30 c.c. of water until dissolved, and then 1 c.c. of a cold saturated solution of potassium dichromate is added and allowed to remain for an hour with occasional shaking. The colour is then compared with that produced in a mixture of the toluidines in known proportions. M. J. S.

Detection of Blood Stains. By LEONE and DENARO (*Gazzetta*, **19**, 97—99).—Old, decomposed stains, from which water will no longer dissolve out the colouring matter, are treated with a solution of potash or soda. If hæmatin is present, it will pass into solution, and the filtered liquid will appear green in a thin layer, and red in a thick layer. The solution will also contain iron, which may be detected in the ash. The evaporation and ignition for this purpose must be conducted in silver, and not in porcelain vessels, since the latter give up an appreciable amount of iron. S. B. A. A.

Detection of the Colouring Matter of the Yolk of Egg. By S. BEIN (*Ber.*, **23**, 421—422).—Thudichum has long since shown that yellow colouring matters, termed by him "luteïnes," can be obtained from the yolk of egg and that these yield with nitric acid a blue coloration, which turns yellow and shows two or three characteristic bands in the spectrum. This reaction has been employed for the detection of egg-substance mixed with other organic matter, but the author shows that the non-formation of this coloration does not prove the absence of egg-substance, as these colouring matters gradually undergo alteration in air and light, more quickly at 60° to 80°, and then cease to give Thudichum's reaction. The formation of the coloration, on the other hand, does not prove the presence of these substances, as other organic compounds, especially certain nitrogenous decomposition-products, give the same reaction. H. G. C.

An Exact Method for the Estimation of Egg-substance. By S. BEIN (*Ber.*, **23**, 423—424).—In the previous abstract it has been shown that the qualitative test hitherto employed for the detection of egg-substance is not trustworthy, and no method of estimating the amount of these substances has been previously published. The present paper gives a method by which the quantitative estimation of these substances may be readily made, depending on the fact that two of the chief constituents of yolk of egg, namely, glycerolphosphoric acid and lecithin, both contain phosphoric acid. These compounds may be extracted with ether, the ethereal solution evaporated, and the residue carefully ignited at a low temperature with a fragment of potassium nitrate, and the residual phosphoric acid weighed. Lecithin has been shown to consist of an ether-like compound of neurine and distearylglycerolphosphoric acid, having the formula $C_{44}H_{90}NPO_9$, and according to Gobley (*Annalen*, **60**, 275), yolk of egg contains 1·2 per cent. of glycerolphosphoric acid and 7·2 per cent. of lecithin. Every 1·12902 grams of phosphoric acid found, therefore, represents 100 grams of yolk of egg. H. G. C.

General and Physical Chemistry.

New Form of Gas Battery. By L. Mond and C. Langer (*Proc. Roy. Soc.*, **46**, 296—304).—The form described may be termed a *dry* gas battery. A diaphragm of a porous, non-conducting material, mostly plaster of Paris, is impregnated with dilute sulphuric acid (or other electrolyte), and covered on both sides with thin platinum-foil containing about 1,500 perforations per square centimeter, which is overlaid in its turn by a film of platinum-black. The foil is placed in contact at small intervals with strips of a good conductor, so as to reduce the internal resistance to a minimum. Diaphragms so prepared are placed side by side or one above the other, with non-conducting frames intervening in such a way as to form chambers through which the gases to be employed are passed. One side of each diaphragm is exposed to one gas (air); the other to the other gas (hydrogen), the spaces between the diaphragms being so connected that the gases pass through the whole series.

The electromotive force of such a battery was found to vary considerably with the quality of the platinum-black. The best results were obtained with a material precipitated from a boiling solution of platinum tetrachloride, neutralised with sodium carbonate, and reduced by a boiling solution of sodium formate. In this case, the electromotive force was 0·97 volt. The resistance of a plate of plaster of Paris 8 mm. thick and of 350 sq. cm. surface was observed to be 0·02 ohm. Experiment showed that the maximum amount of work was obtained when the external resistance was nearly double the internal resistance. Practically, it was found most convenient to work the battery with an electromotive force of about 0·73 volt, which allows a current of 2—2·5 ampères to be taken out of an element with 700 sq. cm. active surface, covered with 0·35 gram of platinum-foil and 1 gram of platinum-black. No less than half the energy of combustion of the hydrogen is converted into electrical energy. It seems to make little difference whether oxygen and hydrogen are employed, or air and a gas containing about 30—40 per cent. of hydrogen (such as can be got by the action of steam, with or without air, on coal, coke, &c.). The temperature should be kept constant at 40° by passing excess of air through the battery.

The authors discuss the cause of the divergence of the electromotive force from the value it should have according to Thomson's theorem, which would indicate an electromotive force of 1·47 volts. The battery exhibits polarisation after having been at work for some time. This is caused by a change in the concentration of the acid at the two electrodes, and may be remedied by interchanging the gases from time to time. (See next abstract.) J. W.

Air Batteries. By C. R. A. Wright and C. Thompson (*Proc. Roy. Soc.*, **46**, 372—376).—The authors direct attention to a former

paper by them (*Proc. Roy. Soc.*, **44**, 182), and point out that the gas batteries there described are practically identical in principle with that described by Mond and Langer (see preceding abstract). They further indicate that many of the results obtained by the latter are in complete agreement with experiments of their own. J. W.

Chemistry of Storage Batteries. By E. FRANKLAND (*Proc. Roy. Soc.*, **46**, 304—308).—In continuation of a former paper (Abstr., 1883, 839), the author describes some experiments undertaken with a view to ascertain what lead compounds actually take part in the chemical reactions on charging and discharging secondary batteries.

Finely powdered lead oxide was treated with successive portions of dilute sulphuric acid until the liquid exhibited a permanent acid reaction. There resulted a buff-coloured powder having the composition $Pb_5S_3O_{14}$. Red lead (Pb_3O_4) treated in the same manner yielded a brownish-red compound corresponding with the formula $Pb_3S_2O_{10}$. These new salts must constitute the original active material of storage cells formed in the above way, so that the following equations will represent the actions at the different plates on charging and discharging.

If the buff salt is the active material, then we have—

I. On charging.

(*a.*) Positive plates.. $Pb_5S_3O_{14} + 3H_2O + 5O = 5PbO_2 + 3H_2SO_4$.

(*b.*) Negative „ .. $Pb_5S_3O_{14} + 5H_2 = 5Pb + 3H_2SO_4 + 2H_2O$.

II. On discharging.

(*a.*) Positive plates.. $5PbO_2 + 3H_2SO_4 + 5H_2 = Pb_5S_3O_{14} + 8H_2O$.

(*b.*) Negative „ .. $5Pb + 3H_2SO_4 + 5O = Pb_5S_3O_{14} + 3H_2O$.

If the red salt is the active material, the equations become—

I. On charging.

(*a.*) Positive plates.. $2Pb_3S_2O_{10} + 2O_2 + 4H_2O = 6PbO_2 + 4H_2SO_4$.

(*b.*) Negative „ .. $Pb_3S_2O_{10} + 4H_2 = 3Pb + 2H_2SO_4 + 2H_2O$.

II. On discharging.

(*a.*) Positive plates.. $6PbO_2 + 4H_2SO_4 + 4H_2 = 2Pb_3S_2O_{10} + 8H_2O$.

(*b.*) Negative „ .. $3Pb + 2H_2SO_4 + 2O_2 = Pb_3S_2O_{10} + 2H_2O$.

The latter alternative would seem to explain the practical observation that only half as much active material is required on negative as on positive plates. J. W.

Electromotive Force of Metallic Salts. By C. L. SPEYERS (*Amer. Chem. J.*, **12**, 254—261).—Solutions of hydrochloric, nitric, acetic, and sulphuric acids, and of the zinc salts of these acids, were experimented with, as well as solutions of these salts containing free acid; the solutions contained 1 gram equivalent of each substance in from 1 to 24 litres of water. In these solutions were immersed an amalgam of mercury containing 1 per cent. of zinc, serving as the negative plate, and a globule of mercury, serving as the positive; connection was made with an electrometer, and the electromotive force was measured as soon as it had attained a constant value. The electromotive force increases slightly on dilution. It has approximately the same value in solutions of nitric, acetic, and sulphuric acids of equivalent strength, but a lower value in the case of hydrochloric acid; and in the case of a mixture of hydrochloric with one of the other acids, the electromotive force is little greater than with hydrochloric acid alone. The electromotive force of solutions of the zinc salts is considerably less than that of equivalent solutions of the corresponding acids, and the chloride has a lower electromotive force than the nitrate, acetate, and sulphate. In the case of concentrated mixtures of zinc salts, and of mixtures of salts with free acid, the electromotive force has a value but slightly greater than in the case of the constituent of lower value. The electromotive force of $\frac{1}{2}ZnR + HR'$ is equal to that of $\frac{1}{2}ZnR' + HR$; the agreement is not satisfactory, however, in the case of zinc nitrate and sulphuric acid.

C. F. B.

Rate of Solution of Carbonates in Acids. By W. SPRING (*Bull. Soc. Chim.* [3], **3**, 174—177).—At 15°, the rates of solution of the following carbonates in 10 per cent. hydrochloric or nitric acid are:—Iceland spar, 1; witherite, 1·284; cerusite, 0·757; arragonite, 0·476; azurite, 0·334; malachite, 0·231; smithsonite, 0·087; dolomite, 0·025. The individual carbonates dissolve with equal rapidity in each acid of the strength indicated; increase of temperature causes an increased rate of dissolution which varies for each mineral, and no definite law appears to hold; the rate of solution seeming to be independent of their chemical constitution, but dependent on varying physical factors.

T. G. N.

Rate of Solution of Iceland Spar in Hydrochloric Acid. By W. SPRING (*Bull. Soc. Chim.* [3], **3**, 177—184; compare Abstr., 1888, 900).—The rate of solution of separate faces of Iceland spar is not only dependent on the chemical nature of the spar, but also on its elasticity, and the velocity of solution is expressed by the equation

$$v = \sqrt{a^2 \sin^2 \varphi + c^2 \cos^2 \phi};$$

a = the minimum elasticity = 0·60294; c = the maximum elasticity = 0·6728; and ϕ = the angle made by the face attacked with the optic axis, which for the cleavage plane is 26° 15′ 14″.

The variation in velocity is affected by the temperature, and is represented by the expression

$$v = u\,(0{\cdot}001T^2 + 0{\cdot}775).$$

The experimental data agree closely with the calculated values.

T. G. N.

Change of Volume on Dissolving Salts in Water. By G. C. SCHMIDT (*Monatsh.*, **11**, 35—41).—On dissolving a salt in water, or on diluting a salt solution, a contraction takes place in the total volume. From this it follows that the volume occupied by a molecule of the salt must be less when in solution than when in the solid state, and less in a dilute than in a concentrated solution.

The molecular volume of a salt when in solution may be calculated by means of the formula $V = (aq - \alpha)/d - aq/\delta$, where α is the molecular weight of the anhydrous salt, aq the weight of water present to each molecule of the salt, d the density of the salt solution, and δ that of water. If p is the percentage of anhydrous salt in the solution, then $aq = (100 - p)\alpha/p$.

Employing this formula, it will be found that the molecular volume of a dissolved salt decreases with rising dilution, until at length a limit is reached at which it remains practically constant. This is rendered evident by the following two examples :—

KCl at 18°.		Cane-sugar at 17·5°.	
Per cent. of dissolved salt.	Mol. vol.	Per cent. of dissolved sugar.	Mol. vol.
21	34·95	50	214·49
10	30·06	20	210·60
5	30 02	5	209·95
3	29·98	3	209·88
2	29·97	2	209·85
1	29·97	1	209·83

To account for this behaviour, the author assumes that in the case of salts like potassium chloride, which are electrolytes, it is due to the dissociation of the salt into its ions, which increases and approaches a limit with rising dilution ; and that in the case of non-electrolytes like cane-sugar, it is probably due to the fact that complex molecules exist in the concentrated solutions which are broken up on increasing the dilution.

Arrhenius has shown that in a dilute solution the molecular volume of an electrolyte should be an additive function of those of its two ions. If an electrolyte having the ions x and y is dissolved in water, the volume of the resulting solution becomes $1 + ax + by$, where a and b are constants depending on the nature of the ions, but quite independent of one another. In like manner, for any other electrolyte with the ions s and t, the volume would become $1 + cs + dt$, the constants in this case being c and d. If the equivalent weights of the ions in the above instances are given by x, y, s, and t, then the molecular volume of the electrolyte in the first case is $a + b$, and in

the second $c + d$, and if one of the ions in the two electrolytes happens to be the same, that is, if $a = c$ or $b = d$, then either $b - d$ or $a - c$ = const.

In order to test the above relation, the author has calculated the molecular volumes of a number of electrolytes when in solution, using for this purpose the density determinations of Kohlrausch, Kremer, and Gerlach. The numbers are calculated for 5 per cent. solutions at a temperature of 18°, and are given in the following table :—

Salt.	Mol. vol.	Salt.	Mol. vol.
KCl	30·02	NH_4Cl	38·51
KI	47·80	NH_4I	58·21
KBr	37·00	NH_4NO_3	50·19
KNO_3	41·69	$LiCl$	19·82
$KC_2H_3O_2$	54·38	LiI	40·69
K_2SO_4	48·69	$BaCl_2$	30·76
$NaCl$	19·49	$Ba(NO_3)_2$	56·65
NaI	37·70	$CuCl_2$	15·89
$NaNO_3$	31·20	$Cu(NO_3)_2$	41·74
Na_2SO_4	19·00	$SrCl_2$	24·01
$NaC_2H_3O_2$	43·66	$Mg(NO_3)_2$	40·30

Reference to the above table will show that the differences $KCl - NaCl$, $KI - NaI$, $KNO_3 - NaNO_3$, $KC_2H_3O_2 - NaC_2H_3O_2$ are all approximately equal to 10, and also that $K_2SO_4 - Na_2SO_4 = 19·69$. Then again $KCl - KI$, $NaCl - NaI$, $LiCl - LiI$ all approximate to -20; and it will be evident from other cases which might be selected that the molecular volumes of electrolytes are made up of two constants, one of which depends on the positive and the other on the negative ion. One or two exceptions were noted to this rule, but these are explained by the fact that the salts with which they occurred are poor conductors and not fully dissociated in a 5 per cent. solution.

H. C.

The Nature of Solutions. By S. U. Pickering (*Phil. Mag.* [5], **29**, 427—434).—This paper is a *résumé* of one which appeared in the Trans., 1890, 64, special attention being directed to those points which the author considers refute Arrhenius' objections (*Phil. Mag.*, **28**, 36) to his conclusions.

S. U. P.

Deductions from Van't Hoff's Theory. By S. Pagliani (*Gazzetta*, **19**, 235—251).—In the equation $PV = iRT$ applied to solids in dilute solution, Arrhenius considers i to be the ratio between the absolute pressure exercised by a substance in solution and that which it would exercise if no dissociation took place; for extremely dilute solutions, i therefore equals unity, and for other dilute solutions, it is taken as equal to the ratio (α) of the effective molecular electric conductivity to the limiting value of that conductivity with increasing dilution; from these assumptions, Arrhenius deduces the formula

$i = 1 + (k - 1)\alpha$, where k is the number of ions into which each active (that is, dissociated) molecule is split up (Abstr., 1887, 631).

The author objects to this formula on the grounds that some electrolytes have a maximum electrical conductivity, so that the equation is inapplicable, and that k is a variable quantity, its value depending on the conditions of dilution and temperature of the solution of the electrolyte. The equation also indicates that when $i = 1$, $k = 1$, which is untrue for many conductors, also as for binary compounds $k = 2$, and $\alpha = 1$ when dissociation is complete, $i = 2$ at that stage, a result disproved by Raoult's experiments on HCl, HBr, HI, NaCl, KBr, KI. The agreement of many of the values of i calculated by Arrhenius from the molecular depressions with the values calculated from α is only apparent since the calculations were not made from solutions of the same degree of concentration.

The objections to the determination of i from the formula $i = \frac{t}{18{\cdot}5}$, from Blagden and Rüdorff's law, from the diminution of vapour tension, and from the isotonic coefficient are also discussed.

The heat of solution of a gas may be determined either from Van't Hoff's equation, $\frac{\delta \log C}{\delta T} = \frac{Q}{2iT^2}$, which becomes $Q = 2T^2\frac{\delta \log C}{\delta T}$ when $i = 1$ (where C is the concentration of a solution saturated at temperature T, and Q is the quantity of heat absorbed by the solution of one molecule of the substance), or from Kirchoff's equation $q = -g\frac{RT^2}{J}\frac{\delta \log \beta R}{\delta T}$ or $Q = \frac{MRT^2}{J}\frac{\delta \log \beta R}{\delta T}$ (*Pogg. Ann.*, **103**, 194), where R is the constant for the gaseous state, and β is the weight of gas absorbed by the unit of weight of liquid at the temperature T and a pressure equal to unity, so that βR is Bunsen's coefficient of absorption. These equations give concordant results for perfect gases (where $i = 1$), but not where the state of the gas is changed as by absorption, diffusion, or by particular conditions of temperature and pressure. The great discrepancies between the theoretical values of Q so deduced and the values obtained by experiment are, according to the author, due to the neglect in Kirchoff's equation of the molecular work done during dissolution, to the variable value of i in Van't Hoff's equation, and to a less extent to the variation of the heat of dissolution with the concentration of the solution. The author then discusses the determination of the value of i for solids in solution from Van't Hoff's equation in the form $i = Q \div \frac{2\delta \log C}{\delta T}T^2$, and the conditions of applicability of this formula. S. B. A. A.

The Theory of Osmotic Pressure. By S. U. Pickering (*Phil. Mag.* [5], **29**, 490—501).—Without questioning the practical utility of this theory, the author doubts whether it can be regarded as sufficiently well established to give any support to a purely physical theory of solution. Taking the lowering of the freezing point of a solvent by the addition of dissolved matter as the most fully investigated phenomenon connected with osmotic pressure, he shows that the

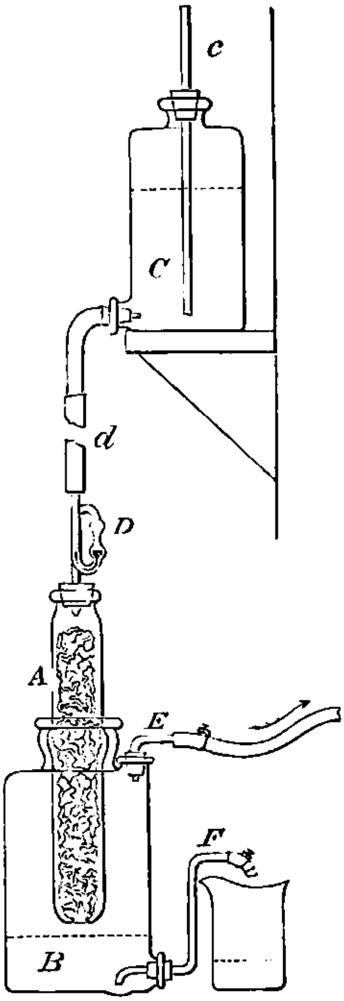
depression (produced by 1 foreign molecule on 100 solvent molecules), instead of being constant whatever the dissolved substance is, exhibits a variation amounting to 500 per cent. in extreme cases, even when very weak solutions are taken. He argues that the higher values must be taken as being the "normal" values in the case of water, just as they are in the case of other solvents, especially as the assumption that the lower value (1·03°) is the normal one involves the rejection of the atomic theory, since it is $1\frac{1}{2}$ times the normal value for other solvents, and could only be explained by assuming that the molecule of water is $1\frac{1}{2}H_2O$. The smaller value being the normal one, necessitates, moreover, the view that salts and acids are entirely dissociated into their ions in weak solutions, and such a view must lead to the conclusion that the more stable a body is, the more easily is it dissociated, and that in the dissociation we have an actual creation of energy; a conclusion which is quite inadmissible. Instances are quoted to show that the nature of solvent, instead of being without effect on the so-called constant, causes it to vary by amounts up to 27,600 per cent. The constancy, moreover, does not hold good when the proportions of the solvent and dissolved body are varied, even when the variations are confined to solutions so weak that the dissolved body is as much dilated as it would be if it were gaseous, and the deviations from regularity in such cases do not occur in any regular manner or direction. Finally, that, whereas, according to the osmotic pressure theory, strong solutions should give abnormally small values for the depression, they give, in every case at present investigated, abnormally large ones. S. U. P.

Precipitation. By G. WATSON (*Chem. News*, **61**, 207—208).—With regard to the accumulation of precipitates on scratches made on the sides of the glass containing vessel, experiments with basic antimonious chloride and with calcium hydrogen phosphate have led to the following observations:—The phenomenon does not take place until the precipitate, at first bulky, changes into the denser crystalline condition; neither does it take place on new scratches made after change is complete, nor on old scratches which have been washed with acid. But old scratches with crystals adhering, are capable of starting and accelerating the formation of the crystalline precipitate, in the same way as the presence of previously formed precipitate will aid precipitation, as shown by Baubigny in the case of nickelous sulphide, and now by the author in the case of the precipitation of arsenic as sulphide from warm solutions of phosphoric acid. Hence, the author concludes that the phenomenon in question is not alone the result of the potent surface energy of abraded glass, but is also due to the simultaneous occurrence of a condensation change.

D. A. L.

A Self-regulating Gas-generator. By H. W. HILLYER (*Amer. Chem. J.*, **12**, 228—230).—This consists of an acid reservoir, C, and a generator, AB. The former is an aspirating bottle of a gallon or more capacity, provided with a stopper and glass tube, *c*, to regulate the liquid pressure. A piece of stout indiarubber tubing connects it to the bulb-tube D, which passes through a rubber stopper in the

cylinder A, and terminates in a narrow aperture $\frac{1}{16}$th of an inch in diameter. The generator consists of a glass cylinder, A, and a glass vessel, B, which are ground or cemented together gas-tight. The cylinder A is about 20 inches long by $2\frac{1}{2}$ in diameter, and serves to



hold the ferrous sulphide, zinc, or marble. The vessel B is about 18 inches high by 9 in diameter, and serves as a reservoir both for waste acid and for gas. The acid flows down into A, and by the pressure of the gas generated is forced over the contents of the cylinder and into the vessel B, the gas escaping through the tube E. When E is closed, the pressure in the generator rises and soon becomes great enough to stop the flow of acid through *d*D. A too sudden rise of pressure, which might force the acid from D*d* back into C, is prevented by the large capacity of the vessel B, and a further safeguard is provided by filling the lower bend of D with mercury. The waste acid drops into B almost neutral, and is forced out through F, on opening the stop-cock, by the pressure of the gas in B. The acid in C is renewed by removing the stopper and tube *c*, and the cylinder A is refilled by removing its rubber stopper, after closing the pinch-cock on *d*. The generator is connected to a series of gas-cocks placed in

the laboratory through two wash-bottles which have their long tubes joined together; this device is necessary to prevent the water in the wash-bottle being driven back into the generator B. in consequence of the lowering of pressure caused in this vessel when the waste acid is removed through F. The apparatus supplies gas at a considerable pressure, and it is therefore necessary that all the joints should be gas-tight. C. F. B.

Inorganic Chemistry.

Rate of Decomposition of Chlorine-water by Light. By G. Gore (*Proc. Roy. Soc.*, **46**, 362—363).—By studying the action of diffused daylight and sunlight on chlorine-water by means of the voltaic balance, the author finds that the decomposition at first takes place with moderate uniformity and gradually diminishing decrease of voltaic energy. At the minimum, the liquid contains only hydrochloric, hypochlorous, and chloric acids. On further exposure, the voltaic energy increases slowly until the solution contains only hydrochloric acid and hydrogen peroxide. Thus there are here two essentially different periods of chemical change—first, the period of the formation of oxygen acids of chlorine, and second, the period of the decomposition of these acids into hydrochloric acid, and hydrogen peroxide. J. W.

Igniting Point of Sulphur. By J. R. Hill (*Chem. News*, **61**, 125—126); and by B. Blount (*ibid.*, 153—154).—Hill concludes from experimental observations that sulphur ignites at 248°. In his experiments, the sulphur contained in a test-tube, fitted with a double bored cork, was heated in a bath of sulphuric acid, while a current of air, heated to about 60,° was aspirated through the sulphur-tube. Blount, under somewhat similar circumstances, found the igniting point of sulphur to be 261°, but owing to the supply of air being very limited, this number is probably too high. D. A. L.

Simple and Rapid Preparation of Pure Gases. By H. Bornträger (*Zeit. anal. Chem.*, **29**, 140).—Instead of using an acid for the evolution of carbonic anhydride, sulphurous anhydride, and similar gases, it is convenient to use sodium hydrogen sulphate. A mixture of equivalent quantities of the respective salts in powder gives, when wetted with water, a regular stream of the required gas, which will be free from the impurities usually derived from the use of an acid. M. J. S.

Silver Silicate. By J. D. Hawkins (*Amer. J. Sci.* [3], **39**, 311—312).—This salt forms as a yellow precipitate when pure sodium silicate is added to a neutral solution of a silver salt. When heated, it becomes first brownish-red, then the original yellow, and at a

red heat decomposes into silver, oxygen, and silica. It is soluble in ammonia, and is decomposed by all acids. D. A. L.

Dimorphism of Barium Oxide: a New Catalytic Phenomenon. By G. BRÜGELMANN (*Zeit. anal. Chem.*, **29**, 123—126).—Barium oxide, prepared by strongly heating the hydroxide in clay or graphite crucibles, is obtained as a felted mass of elastic needles, which, since they show chromatic polarisation, cannot belong to the regular system, but are probably hexagonal. Their specific gravity is 5·32 (water at 15° = 1). The same hydroxide, when dehydrated in a platinum crucible, yields an oxide which, although distinctly crystalline, shows no polarisation, and therefore seems to belong to the regular system. It has the specific gravity 5·74, and appears to be identical with that produced by igniting the nitrate (Abstr., 1880, 701). M. J. S.

Characteristics of the Alkaline Earths and Zinc Oxide. By G. BRÜGELMANN (*Zeit. anal. Chem.*, **29**, 126—129; see Abstr., 1880, 701).—Recent experiments have shown that the magnesium oxide obtained by igniting the nitrate is not amorphous, but crystalline. Strontium oxide is also crystalline when prepared by the ignition of the carbonate or hydroxide. Strontium and barium oxides prepared in platinum crucibles are pure white, not grey, as hitherto believed. Barium hydroxide is decomposed at a much lower temperature than the carbonate, but between these limits of temperature barium oxide does not absorb carbonic anhydride. The specific gravities of the oxides vary slightly according to the compounds from which they are obtained, but, with the exception of barium oxide, no evidence of dimorphism has been obtained. M. J. S.

Atomic Weight of Magnesium. By W. M. BURTON and L. D. VORCE (*Amer. Chem. J.*, **12**, 219—226).—The method used was similar to that formerly adopted in determining the atomic weight of zinc (Abstr., 1888, 1247). Magnesium ribbon was placed in a short length of iron tubing, and this was placed in the closed end of a longer tube of very hard glass. The tube was exhausted, and the magnesium was then distilled into the fore part, and the whole allowed to cool while the vacuum was still maintained. A slight coating of magnesium silicide formed at first on the tube, but this protected the glass, and the rest of the metal which distilled over could be easily detached, and was free from silicide. The middle part of the distilled metal was taken, and redistilled three times in a similar manner; a crystalline bar of pure white magnesium was thus obtained free from silicon, carbon, calcium, and iron, although these could be detected in the ribbon used. The purified metal was dissolved in nitric acid (prepared as described in the previous paper), diluted with an equal volume of specially purified water; the excess of water was then evaporated, and the nitrate converted into oxide by heating first in a sand-bath, and finally in a muffle furnace. The operation was performed in a porcelain crucible, previously tared against another one which was treated in precisely the same way as

the first. Ten experiments were made, and these gave for the atomic weight of magnesium numbers varying between 24·271 and 24·304, the mean being 24·287 (O being taken as 16).

In some cases very perfect crystals were obtained when the magnesium was distilled. These were examined by G. H. Williams, and found to be holohedral hexagonal forms isomorphous with those of zinc and beryllium. They exhibited faces of the primary prism and of the primary pyramid, together with basal planes; the axial ratio was determined to be $a : c = 1 : 1·6202$. C. F. B.

Crystalline Metallic Precipitates. By H. N. WARREN (*Chem. News*, **61**, 183).—By using a zinc rod wrapped in coils of asbestos paper for the reduction of solutions of metallic salts, the action is somewhat retarded, and a crystalline precipitate of the reduced metal forms without any previous spongy precipitate, and adheres to the asbestos paper. In this way, crystalline precipitates of lead, copper, &c., have been obtained, whilst by the use of a magnesium rod crystalline zinc was precipitated, and iron, manganese, and zirconium gradually reduced. Solutions of antimony chloride, with sufficient tartrate to prevent the precipitation of the basic salt, yield, in addition to a crystalline incrustation, a black precipitate of explosive antimony. D. A. L.

Copper Precipitate formed in Ordinary Water. By GRIMBERT and BARRÉ (*J. Pharm.* [5], **21**, 414—415).—A solution of copper sulphate poured into ordinary water produces a considerable turbidity, which becomes a voluminous, bluish-green, crystalline deposit after a time. Under the microscope, it shows rhomboidal laminæ which polarise light; these are sometimes isolated, sometimes grouped in stars of six branches. It is a tetrabasic copper sulphate, $3CuO,CuSO_4 + 4H_2O$, insoluble in water, but soluble in acids. Heated at 100° it is unchanged, but towards 200° the whole of its water is expelled, and its colour becomes olive green. It has the same composition as the mineral brochantite. The deposit is inferred to be due to the presence of calcium hydrogen carbonate in the water, as very dilute alkaline carbonates are known to precipitate tetrabasic copper sulphate, and no precipitate is produced if the hydrogen carbonate is removed. J. T.

Earths of the Cerium and Yttrium Groups. By A. BETTENDORFF (*Annalen*, **256**, 159—170).—Orthite, from Strömsboe, near Arendal, and from Hitteroë, was freed from cerium oxide and thorium oxide by Debray's method (*Compt. rend.*, **96**, 928), and the earths of the cerium and yttrium groups then separated by means of potassium sulphate, by a modification of the method described by Mosander. The separation of the constituents of the two groups was then accomplished by systematic partial decomposition of the nitrates; this can be easily done with the nitrates of the yttrium group, but in the case of the cerium group it is advisable to place the platinum crucible containing the nitrates in a slightly larger porcelain crucible, in order to ensure a more regular decomposition. In this way the

earths which are precipitated by potassium sulphate can be easily freed from lanthanum by two or three operations; the lanthanum oxide obtained is very pure (RO = 108·76), but it always contains small quantities of didymium.

The basic nitrates thus freed from lanthanum give a brown oxide (RO = 113·2 to 114), which contains all the didymium and samarium earths, as well as larger or smaller quantities of gadolinium and terbium earths.

The further purification of the oxide (RO = 108·76) was carried out by v. Welsbach's method (*Monatsh.*, **6**, 477—491), namely, by fractional crystallisation of the ammonium nitrate double salts, but in neutral instead of in acid solution. After about 18 operations, the ammonium lanthanum nitrate is obtained in a pure condition, and the double salt of the neodidymium is separated from the more sparingly soluble double salt of the praseodidymium, as is shown by a spectroscopic examination of the mother liquors; the absorption spectra of the second, seventh, twelfth, and eighteenth mother liquors are given in a diagram.

The oxide of the pure lanthanum ammonium nitrate, prepared as described above, has the equivalent RO = 108·15, R_2O_3 = 324·45 (O = 15·96, S = 31·98), from which the atomic weight of lanthanum is found to be R = 92·19, or R''' = 138·28; Cleve (*Jahresb.*, 1883, 36) found R''' = 138·22. The spark spectrum of the chloride, prepared from this oxide, is given in a diagram, and the measurements of the wave-lengths of the lines are given in a table; the author's measurements agree well on the whole with those of Thalèn, but some of Thalèn's lines could only be observed with difficulty. λ 4330, which has been observed by Thalèn, but which, according to Cleve, is not a lanthanum line, was present in the spectrum of the author's preparation. F. S. K.

Uranyl Chromate and its Double Salts. By J. FORMÁNEK (*Annalen*, **257**, 102—116).—*Uranyl potassium chromate*,

$$2(UO_2)CrO_4,K_2CrO_4 + 6H_2O,$$

is obtained by mixing a solution of uranyl nitrate (1 mol.) with a solution of potassium chromate (1 mol.), and evaporating over sulphuric acid, or by treating potassium uranate with a warm, concentrated solution of chromic acid and evaporating the filtered solution over sulphuric acid. It forms yellow, monosymmetric crystals, $a:b:c$ = 0·7566 : 1 : 1·9714, β = 72° 38′, and is partially decomposed by water. The corresponding *ammonium* double salt,

$$2(UO_2)CrO_4,(NH_4)_2CrO_4 + 6H_2O,$$

forms yellow, monosymmetric crystals, $a:b:c$ = 0·8016 : 1 : 1·0196, β = 72° 31′, similar to those of the potassium salt, and is partially decomposed by boiling water; the compound $2(UO_2)CrO_4,(NH_4)_2CrO_4 + 3H_2O$ was also obtained. The *sodium* double salt,

$$2(UO_2)CrO_4,NaCrO_4 + 10H_2O,$$

forms small, yellow crystals, and is readily soluble in water.

Uranyl chromate, $(UO_2)CrO_4 + 11H_2O$, prepared by dissolving the hydroxide in an aqueous solution of chromic acid, and concentrating the filtered solution on the water-bath, crystallises from boiling water in yellow needles, effloresces on exposure to the air, and loses the whole of its water at 200°; only silver, lead, mercurous, and bismuth salts produce precipitates in its aqueous solution.

In precipitating chromic acid as mercurous chromate, in presence of uranium salts, the mercurous nitrate employed must be free from oxides of nitrogen, and the solution must be slightly acid; otherwise some of the uranium salt is also precipitated.

When hydrogen sulphide is passed into a solution of uranyl nitrate and mercurous nitrate, mercuric sulphide is precipitated, and at the same time the uranyl is reduced to the uranous salt; tungstates and titanates are also quickly reduced by hydrogen sulphide in presence of mercuric chloride. F. S. K.

Precipitation of Tin from Acid Solutions by Metallic Iron. By B. Schultze (*Ber.*, **23**, 974—976).—Tin is completely precipitated from solution in inorganic acids by the action of a mixture of metallic tin, metallic iron, and iron rust. The free acid is neutralised by the ferric hydrate, the stannic salts which are simultaneously formed are reduced by the tin to stannous compounds, and from these all the tin is thrown down by the iron. The operation requires several days for completion, and the absence of every trace of free acid and stannic salt is essential to success. J. B. T.

Mineralogical Chemistry.

Deposits of Barium Sulphate from Mine-water. By F. Clowes (*Proc. Roy. Soc.*, **46**, 368—369).—Deposits containing some 90 per cent. of barium sulphate have been found in the water-boxes of various coal mines in the neighbourhood of Newcastle-upon-Tyne. The author publishes the results of his analyses of three of these, and discusses their probable mode of formation. J. W.

Tyrolite from Utah. By W. F. Hillebrand and E. S. Dana (*Amer. J. Sci.*, **39**, 271—273).—Analysis of material collected at the Mammoth mine gave the following results:—

CuO.	CaO.	As_2O_5.	H_2O.	SO_3.	Fe_2O_3.	Insoluble.	Total.
45·08	6·78	28·52	17·21	2·23	0·08	0·16	100·06

The percentage of SO_3 is practically the same as that formerly found by Hillebrand (Abstr., 1888, 1043). It is, therefore, necessary to consider this as a proper constituent of the mineral. Some of the specimens of tyrolite collected are crystallised with sufficient distinct-

ness to allow of a somewhat more complete determination of the form than has hitherto been possible. The crystals are undoubtedly orthorhombic. B. H. B.

Occurrence of Polycrase in Carolina. By W. E. HIDDEN and J. B. MACKINTOSH (*Amer. J. Sci.*, **39**, 302—306).—A few crystals of the mineral described were found in 1888 in Henderson Co., North Carolina, the associated minerals being zircon, monazite, xenotime, cyrtolite, and magnetite. The pure mineral is nearly coal-black, and has a sp. gr. of 4·78 and a hardness of 5·5. It is infusible, and on analysis yielded :—

Nb_2O_5. Ta_2O_5. TiO_2.	Y_2O_3.	Fe_2O_3.	UO_3.	H_2O.	Total.
48·97	27·55	3·19	13·77	5·18	98·66

The reactions are quite similar to those given by the Hitteroë polycrase.

In September, 1889, large crystals of polycrase were found near the Upper Saluda River, in South Carolina, about 20 miles from the first described locality. The sp. gr. of these crystals varies between 4·925 and 5·038. On analysis the following results were obtained :—

Nb_2O_5. Ta_2O_5. TiO_2.	Y_2O_3.	PbO.	FeO.	Fe_2O_3.	UO_3.
47·88	21·23	0·46	2·47	0·18	19·47

CaO.	H_2O.	SiO_2.	Insoluble.	Total.
0·68	4·46	1·01	0·12	97·96

This mineral is very closely allied to, if not identical with, the polycrase from Hitteroë, Norway, analysed by Rammelsberg. The approximate formula of the Carolina mineral is $Nb_2O_5,4TiO_2,5RO,2\frac{1}{2}H_2O$. It should be noted that this is the first occurrence of a columbotitanate accredited to an American locality. B. H. B.

Manganiferous Spring waters. By W. P. MASON (*Chem. News*, **61**, 123).—Sixty-two springs in the United States are reputed to contain manganese, usually as carbonate, but only seven have as much as nine parts per million or above, and in five of these the manganese is present as sulphate or chloride, whilst its condition in the other two is doubtful. Excelsior Springs, near Kansas City, Mo., are, however, comparatively rich in manganese carbonate, yielding per million:—$MnCO_3$, 9·41; Al_2O_3, 2·10; SiO_2, 12·0; K_2SO_4, 4·86; NaCl, 17·60; $FeCO_3$, 23·43; $CaCO_3$, 362·75; $MgCO_3$, 54·7; KCl, 2·8; $NaHCO_3$, 9·35. D. A. L.

Organic Chemistry.

The Marsh Gas Fermentation. By BERTHELOT (*Bull. Soc. Chim.* [3], **3**, 331).—According to Schloesing, marsh gas and carbonic anhydride are formed in equal volumes when dung ferments. Since these gases must result chiefly from the decomposition of cellulose, their formation may be represented by the following equation :—

$$nC_6H_{10}O_5 + nH_2O = 3nCO_2 + 3nCH_4.$$

This equation necessitates the liberation of as much heat as is represented by $41 \times n$ Cals., which is slightly superior to that liberated in the alcoholic fermentation. T. G. N.

Double Cyanides of Zinc and Mercury. By W. R. DUNSTAN (*Pharm. J. Trans.* [3], **20**, 653).—Rammelsberg observed that when zinc sulphate is added to a solution of mercury potassium cyanide, $HgK_2(CN)_4$, a white precipitate is produced. Gmelin suggested that this consists of a cyanide of zinc and mercury, $HgZn(CN)_4$, but no analysis of the precipitate was made by either chemist. During his recent investigation of the antiseptic properties of the metallic cyanides, Sir Joseph Lister prepared this substance, and found it to be of exceptional value as a surgical antiseptic. It was observed, however, that in its preparation the larger part of the mercuric salt is dissolved, especially during the washing of the precipitate with cold water; a smaller part (from 5 to 15 per cent.) remains in the precipitate, and cannot be dissolved from it by cold water.

The author finds that the quantity of mercuric cyanide retained by the precipitate, and not dissolved from it by cold water, is mainly dependent on the amount of water present during precipitation, and that by reducing the quantity to the lowest limit consistent with the solution of the reacting salts, the amount of retained mercuric cyanide may be raised to rather more than 36 per cent., which corresponds approximately with the formula $2Zn(CN)_2,Hg(CN)_2$. Similar results were obtained by precipitating a solution of zinc potassium cyanide, $ZnK_2(CN)_4$, with mercuric chloride, and also by dissolving equivalent quantities of zinc potassium cyanide and mercury potassium cyanide in water, and decomposing the mixed salts with sufficient sulphuric acid to remove the whole of the potassium as sulphate. On the other hand, the same substance was not produced by evaporating to dryness a solution of mercuric cyanide with freshly precipitated zinc cyanide; neither was it obtained by the action of hydrocyanic acid on a mixture of the freshly precipitated oxides suspended in water or alcohol; the product of both these reactions was a mixture of the two cyanides, from which cold water completely dissolved the mercuric cyanide.

Although pure salts were employed in the preparation of the material, a little zinc hydroxy-salt was invariably produced, but experiment showed that the retention of the mercuric cyanide is not

conditioned by the presence of a hydroxy-salt of zinc or mercury. By prolonged boiling with water, the mercuric cyanide is completely removed from the substance. From the evidence so far obtained, the author is inclined to believe that the mercuric cyanide is retained by the zinc cyanide in some mechanical way, and that the substance is not a definite chemical compound. But this question is being further investigated. All attempts to prepare a double cyanide of the formula suggested by Gmelin were failures. W. R. D.

Ammeline. By A. SMOLKA and A. FRIEDREICH (*Monatsh.*, **11**, 42—60; compare Abstr., 1889, 114, and this vol., p. 618).—Ammeline may be synthesised by heating together in a paraffin-bath dicyanodiamide (1 mol.) and ethyl carbamate (2 mols.). The mixture melts at 182—185°, and after heating for a quarter of an hour at 190°, the clear liquid becomes clouded. On raising the temperature to 195° for half an hour, ammeline separates, and may be crystallised from hot aqueous soda, when it forms spherules consisting of microscopic needles. Ammeline is also formed by heating together at 190°, a mixture of anhydrous biguanide sulphate (1 mol.) and ethyl carbonate (4 mols.).

Ammeline is only slightly soluble in water, at 23°, one part in 4677; at 100°, one part in 1260. When freshly prepared it dissolves readily in sulphuric, chromic, oxalic, and in concentrated formic and acetic acids, forming the corresponding salts. The sulphate,

$$(C_3H_5N_5O)_2,H_2SO_4 + H_2O,$$

crystallises in aggregates of very small, microscopic needles, very sparingly soluble in and decomposed by boiling water; the chromate, $(C_3H_5N_5O)_2,H_2CrO_4 + 2H_2O$, crystallises in long, yellow, microscopic needles, is only slightly soluble in, and is decomposed by water; the oxalate, $(C_3H_5N_5O)_2,H_2C_2O_4$, is an anhydrous, white, microcrystalline powder.

The synthesis of ammeline from dicyanodiamide and ethyl carbamate points to its having the constitution represented by the formula $HN<\begin{matrix}C(NH)\cdot NH \\ CO——NH\end{matrix}>CNH$, and thus harmonises with the conclusions drawn by the authors from their synthesis of phenylammeline (*loc. cit.*). G. T. M.

Mixtures of Alcohol and Water. By T. FARRINGTON (*Chem. News*, **61**, 208).—Investigations with mixtures of alcohol and water indicate that the greatest rise of temperature, 10°, is obtained by the admixture of water with 28 to 50 per cent. of alcohol, and the following is the relationship between the densities and refractive indices for the liquids given:—

	Sp. gr.	Refractive index. Observed.	Refractive index. Calculated From formula.	Refractive index. Calculated From vols. of the components.
Alcohol	0·7978	1·3645	—	—
Water	0·9990	1·3320	—	—
5 alcohol + 10 water..	0·9610	1·352	1·3535	1·343
5 alcohol + 5 water...	0·9348	1·361	1·3622	1·348

Whilst a curious relationship exists in the rate of the passage of the liquids through a small aperture, as the following numbers show:—

	Very small aperture. Seconds.	Small aperture. Seconds.
Water................	240	20·9
Alcohol...............	270	22·7
1 alcohol + 2 water....	346	26·9

D. A. L.

The Supposed Hydrates of Alcohol. By S. U. PICKERING (*Zeit. physikal. Chem.*, **6**, 1).—Mendeléeff stated that the first differential of the densities of solutions of alcohol in water which he quoted in the Trans., 1887, 778, formed a rectilineal figure, given on p. 780, showing three distinct breaks, indicative of the existence of three definite hydrates. The author plots out Mendeléeff's values, both those quoted on p. 778, as well as four other sets of values for the density differentials at other temperatures, and shows that they all form curvilinear and continuous figures bearing no resemblance to Mendeléeff's drawing. The author has previously shown (Trans., 1890, 81) that a similar statement made by Mendeléeff as to the densities of sulphuric acid solutions was equally mistaken, and he calls in question Mendeléeff's statement that he had found the rectilineal character of the first differential to hold good in the case of 100 different salts, for Mendeléeff gave alcohol as a "typical" specimen, remarking that "no other solution besides that of alcohol, and none of its other properties, are known with such a degree of accuracy." The author states that he has good grounds for considering that the solid products obtained by Mendeléeff on cooling two solutions of alcohol consisted of ice, and not of two definite hydrates.

The author has examined by differentiation all the values obtained by other physicists for the densities, without finding any evidence of the existence of any hydrates. S. U. P.

Nitrethyl Alcohol. By R. DEMUTH and V. MEYER (*Annalen*, **256**, 28—49; compare Abstr., 1889, 366).—Nitrethyl alcohol has a sp. gr.

of 1·1691 at 19·4°, and its molecular formula is $C_2H_5NO_3$, as is shown by molecular weight determinations in glacial acetic acid solution. The *sodium* salt, $C_2H_4NO_3Na$, is a colourless, granular, hygroscopic powder readily soluble in water; it combines with acetic chloride with great energy, and explodes when treated with concentrated nitric acid.

The compound $N_2Ph·CH(NO_2)·CH_2·OH$ separates as a yellowish-red precipitate when an aqueous solution of the pure sodium salt is treated with a solution of diazobenzene chloride; it crystallises from light petroleum in yellowish-red needles, melts at 104°, and is very readily soluble in the ordinary solvents. When impure nitrethyl alcohol, prepared as previously described, is treated with diazobenzene chloride, benzeneazonitromethane, $N_2Ph·CH_2·NO_2$ (m. p. 153°), separates from the solution in crystals. The formation of this compound is most probably due to the presence of nitracetic acid in the crude nitrethyl alcohol.

Acetylnitrethyl alcohol, $C_4H_7NO_4$, was obtained in an impure condition by warming the pure alcohol with acetic anhydride; it is a yellowish oil, and cannot be distilled even under reduced pressure. The *chloride*, $C_2H_4ClNO_2$, was also obtained, but only in an impure condition, by treating the alcohol with phosphoric chloride in the cold; it is a yellow oil, and cannot be distilled.

Sodionitrethyl alcohol is not acted on by ethyl iodide even when it is boiled therewith, so that its constitution is probably expressed by the formula $NO_2·CHNa·CH_2·OH$.

Nitrethyl alcohol reacts readily both with chloral and phenyl cyanate, but the products cannot be obtained in a pure condition; it is completely decomposed by warm hydrochloric acid and by potassium permanganate. When treated with nitrous acid (1 mol.), it yields methylnitrolic acid as the principal product, but when a large excess of nitrons acid is used, the principal product is an acid free from nitrogen, probably glycollic acid.

When nitrethyl alcohol is reduced with sodium amalgam in slightly acid solution, it is converted into a brown, strongly basic liquid which is miscible with water in all proportions, absorbs carbonic anhydride from the air, and cannot be distilled; the hydrochloride of this substance is a brownish, very hygroscopic syrup. The results obtained on analysis agreed with those required by a mixture of mono- and diethyleneoxydiamine, but it could not be separated into these compounds by the method described by Wurtz (*Annalen*, **121**, 226), and no crystalline salts could be obtained. F. S. K.

Ethereal Salts of Phosphorous Acid. By O. JAEHNE (*Annalen*, **256**, 269—285).—Ethyl phosphite, $P(OEt)_3$, is obtained, together with the compound $C_{14}H_{36}P_2O_8$, described by Geuther (Abstr., 1884, 1282), and a little ethyl phosphate, when phosphorus trichloride is gradually added to finely divided sodium ethoxide, covered with ether; the yield is 70 per cent. of the theoretical. It is a pleasant smelling liqnid of sp. gr. 1·075 at 15°, and boils at 192—195°. When heated with iodine at 190°, it is partially decomposed with formation of ethyl iodide and diethylphosphoric iodide, and when heated with

sodium ethoxide at 150—190°, sodium diethyl phosphite, ethylene, and alcohol are produced. Acetic chloride at 190° seems to decompose it into ethyl chloride, ethyl acetate, and ethyl dihydrogen phosphite; acetic anhydride at 240° seems to have a similar action. When boiled with acetamide, it seems to be converted into the amide of diethylphosphorous acid.

The compound $C_{14}H_{36}P_2O_8$ (see above) is not decomposed by sodium ethoxide at 230°; when treated with phosphorus trichloride, it yields ethyl phosphate, phosphite and chloride, and phosphorous acid.

Methyl phosphite, $P(OMe)_3$, prepared as described in the case of the ethyl salt, is a highly refracting liquid of sp. gr. 1·1785 at 15°, and boils at 185° with considerable decomposition. The *propyl* salt, $P(OPr)_3$, is a yellowish liquid of sp. gr. 1·004 at 15°, and boils at 240° with slight decomposition. The *isobutyl* salt, $P(OC_4H_9)_3$, is a yellowish liquid of sp. gr. 0·952 at 15°, and boils at 248—255°. The *isoamyl* salt, $P(OC_5H_{11})_3$, boils at 265—270°, and its sp. gr. is 0·9005 at 15°. F. S. K.

American Fusel Oil. By J. H. Long and C. E. Linebarger (*Chem. News*, **61**, 185—187).—Most American distillers use corn (maize) mixed with small amounts of other grains for the mash. The authors have examined a sample of fusel oil obtained at Chicago, and separated from alcohol fermented during the spring season by the 72-hour period. It was saturated with water, allowed to settle, dried first with anhydrous copper sulphate, then with potassium carbonate, and fractionally distilled. The higher fractions were separated by fractional crystallisation of the barium amyl sulphates, &c., and identified by their boiling points, optical activity, and conversion into the iodides; whilst the boiling points and conversion into the bromides served for the identification of lower boiling constituents. In this way the sample of several gallons of fusel oil was found to consist chiefly of active and inactive amyl alcohol, with some isobutyl alcohol and isopropyl and ethyl alcohols, and traces of normal propyl and normal butyl alcohols. A very small proportion, consisting of alcohols and ethereal substances, boiled above 133°. D. A. L.

Derivatives of β-Bromopropylamine. By P. Hirsch (*Ber.*, **23**, 964—967).—Propylene-ψ-thiocarbamide, $\begin{matrix} CHMe\cdot S \\ | \\ CH_2\cdot NH \end{matrix}{>}C{:}NH$, is obtained by the action of potassium thiocyanate on β-bromopropylamine; it is identical with the compound obtained by Gabriel (this vol., p. 127) by the action of hydrogen bromide on allylthiocarbamide, and isomeric with trimethylene-ψ-thiocarbamide,

$$CH_2{<}\begin{matrix} CH_2 - S \\ CH_2\cdot NH \end{matrix}{>}C{:}NH.$$

The picrate, $C_4H_8N_2S,C_6H_3N_3O_7$, is deposited from water in curved, needle-shaped crystals melting at 199—200°. The platinochloride forms yellowish-red, needle-shaped crystals melting at 210—212°. Propylene-ψ-carbamide, $\begin{matrix} CHMe\cdot O \\ | \\ CH_2\cdot NH \end{matrix}{>}C{:}NH$, is formed by heating together

β-bromopropylamine and potassium cyanate. The picrate crystallises from hot water in lustrous needles melting at 186°. With carbon bisulphide, β-bromopropylamine yields *μ-β-mercaptomethylthiazoline*, $\begin{array}{l}\mathrm{CHMe{\cdot}S}\\ \mathrm{CH_2{-}N}\end{array}\!\!\geqslant\mathrm{C{\cdot}SH}$, isomeric with μ-mercaptopenthiazoline, $\mathrm{CH_2}<\begin{array}{l}\mathrm{CH_2{-}S}\\ \mathrm{CH_2{\cdot}NH}\end{array}>\mathrm{C{:}SH}$ (this vol., p. 472). The compound crystallises from hot water in long, white needles, and melts at 82°; it is soluble in alkalis, but not in acids. By treating an alkaline solution of mercaptomethylthiazoline with an alkyl iodide, the corresponding thioether is obtained. *Methylmercaptomethylthiazoline*, $\begin{array}{l}\mathrm{CHMe{\cdot}S}\\ \mathrm{CH_2{-}N}\end{array}\!\!\geqslant\mathrm{C{\cdot}SMe}$, is a colourless, oily liquid boiling at 216—218°. The corresponding *ethyl*-compound boils at 228—229°, and the *propyl*-derivative at 246—248°. These compounds are all strong bases, and have an extremely unpleasant odour.

If β-bromopropylamine hydrobromide is warmed with an equivalent quantity of baryta-water, 2 mols. HBr are eliminated, and on distillation a basic substance is obtained of the formula C_3H_7N. It seems to be amidopropylene; it is isomeric with allylamine, from which it is distinguished by giving a crystalline compound with potassium bismuthoiodide. The new base is also isomeric with the two compounds formed by the action of potash on γ-bromopropylamine hydrobromide (compare Abstr., 1888. 1292).

β-Bromopropylbenzamide, $\mathrm{CHMeBr{\cdot}CH_2{\cdot}NHBz}$, is obtained by treating β-bromopropylamine with benzoic chloride in the cold. The amide crystallises from benzene in needles melting at 78°, and if it is dissolved in water, the solution evaporated, and the residue treated with potash, a substance is obtained of the formula $C_{10}H_{13}NO_2$; this crystallises from benzene in white, lustrous leaves, melts at 92—93°, and is most probably *β-hydroxypropylbenzamide*, $\mathrm{OH{\cdot}CHMe{\cdot}CH_2{\cdot}NHBz}$. The same substance is formed by the action of benzoic chloride on the solution, containing β-oxypropylamine, which remains after distilling off the amidopropylene (see above).

On adding methylthiocarbimide to β-bromopropylamine dissolved in benzene, two substances are formed; the one separates as an oil, the other remains dissolved in the benzene. The oily compound is *methylpropylene-ψ-thiocarbamide*, $\begin{array}{l}\mathrm{CHMe{\cdot}S}\\ \mathrm{CH_2{\cdot}NH}\end{array}\!\!>\mathrm{C{:}NMe}$, or

$$\begin{array}{l}\mathrm{CHMe{\cdot}S}\\ \mathrm{CH_2{-}N}\end{array}\!\!\geqslant\mathrm{C{\cdot}NHMe};$$

it solidifies on standing, and crystallises from light petroleum in long needles melting at 49—50°. These crystals are particularly easily soluble in water, and the solution is strongly alkaline. The picrate is obtained in the form of needles melting at 145°. The platinochloride crystallises from water in large, dark-red needles melting at 143°. The second compound is obtained on evaporating the benzene; it is deposited from methyl alcohol in long, white crystals melting at 64°, has the formula $C_7H_{13}N_3S_2$, and is a compound of equal mole-

cules of methylpropylene-ψ-thiocarbamide and methylthiocarbimide. Allylthiocarbimide yields two corresponding compounds: allylpropylene-ψ-thiocarbamide crystallises from light petroleum in quadratic prisms melting at 56°. The picrate is deposited from water in long crystals which melt at 130°. The second product of the action of allylthiocarbimide crystallises from dilute alcohol in white, lustrous prisms melting at 52°. Allylpropylene-ψ-thiocarbamide is also obtained by heating symmetrical diallylthiocarbamide with hydrochloric acid under pressure. An oily, isomeric base, $\begin{matrix} CHMe\text{———}S \\ | \\ CH_2\cdot N\cdot(C_3H_5) \end{matrix}\!\!>\!C{:}NH$, is prepared by the action of allyl iodide on propylene-ψ-thiocarbamide. The picrate crystallises from water in small, triangular prisms melting at 126°. This research shows that the reactions of β-bromopropylamine are completely analogous to those of bromoethylamine. J. B. T.

Tribromopropaldehyde and Tribromopropionic Acid. By L. NIEMILOWICZ (*Monatsh.*, 11, 87—99).—*Tribromopropaldehyde*, $CH_2Br\cdot CBr_2\cdot COH$, is obtained, together with tribromopropionic acid and a liquid polymeride of dibromethylene, on dissolving glycerol in five times its weight of sulphuric acid, treating the solution with hydrobromic acid (sp. gr. 1·49), and heating at 125°. It is an oil which unites energetically with water to form a white, crystalline hydrate, $C_3H_3Br_3O + 2H_2O$, and on heating splits up into hydrobromic acid and the polymeride of dibromethylene above mentioned. The hydrate crystallises in needles or in plates; melts at 61·5°; is only very slowly attacked on boiling with water, yielding a black, humus-like acid product; on oxidation with an equivalent quantity of nitric acid it gives tribromopropionic acid; and yields unsymmetrical dibromethylene, hydrobromic and formic acids on treatment with potash, a decomposition which explains the physiological action of the aldehyde.

Tribromopropionic acid, $CH_2Br\cdot CBr_2\cdot COOH$, is formed in variable quantity, depending on the strength of the hydrobromic acid used and the temperature of the reaction, in the production of tribromopropaldehyde by the method above described. It crystallises from carbon bisulphide in transparent plates, soluble in alcohol, ether, chloroform, and the alkalis, but is scarcely dissolved by water or by dilute acids. It melts at 93°, and forms a sodium salt crystallising with 2 mols. H_2O; a calcium salt crystallising in slender, white needles; and an iron salt, $(C_3H_2Br_3O_2)_3Fe$, crystallising in characteristic red, hexagonal plates. G. T. M.

Aldol. By G. MAGNANINI (*Gazzetta*, 19, 366—367).—Phenylhydrazine acetate precipitates from aqueous solutions of aldol a heavy oil, which, on exposing its ethereal extract for some time in a vacuum, is changed into a transparent, reddish, viscous mass. On heating this substance, it is decomposed, and at a temperature above 160—180°, products pass over which give the pyrazoline reaction with sulphuric acid and potassium dichromate; among these products, aniline and a substance having the odour and reactions of the indoles have been observed. The latter compound is probably the real

hydrazone; it is decomposed by the action of hydrochloric acid in the cold, forming a green colouring matter.

By the prolonged action of hydroxylamine hydrochloride, &c., on aldol, the only product is a mobile, neutral liquid which has the same boiling point as acetaldoxime.

Paraldol is found by Raoult's method to have in acetic solutions the molecular formula $(C_4H_8O_2)_2$. S. B. B. A.

Decahydrated Lead Acetate. By A. E. Fasnacht and C. R. Lindsey (*Chem. News*, **61**, 196—197).—Rhombic plates of the composition $Pb(OAc)_2 + 10H_2O$ have been obtained. Axial ratios, 0·7002 : 1 : 0·9125, observed faces ∞P, $\bar{P}\infty$, $\infty\bar{P}\infty$, $\breve{P}\infty$. They are colourless and transparent, but gradually become opaque and milk-white; they melt at 22·2°, and have a sp. gr. of 1·689. D. A. L.

Conversion of Ethyl Acrylate into β-Alanine. By V. Wender (*Gazzetta*, **19**, 437—440).—Körner and Menozzi have given a method for the formation of unsaturated (olefinoïd) acids by the elimination of nitrogen from the paraffinoïd amido-acids, and have shown that the reaction may be reversed (Abstr., 1887, 1031, 1100), thus obtaining aspartic acid from fnmaric and maleïc acids. To test the latter reaction in the oleïc series, pure ethyl acrylate (15 grams) prepared by Caspary and Tollens' method, by the action of zinc and sulphuric acid on αβ-dibromopropionic acid, was heated with alcoholic ammonia (55 c.c. of 15 per cent.) for 10 hours in a sealed tube at 110—115°. The product was freed from alcohol, dissolved in water, and extracted with ether, the aqueous solution boiled with baryta (24 grams), until no more ammonia was evolved. On removing the barium, the residue yielded on concentration colourless, tabular crystals which, like those of β-alanine, melt with decomposition at 178°, and are very freely soluble in water. To confirm its identity with β-alanine, the product was converted into the copper salt, which crystallises in large, blue tables or prisms, of the composition $(NH_2{\cdot}C_2H_4{\cdot}COO)_2Cu,6H_2O$. This differs from the salt obtained by Heintz (Abstr., 1871, 127) from crude β-alanine, the latter crystallising with only 5 mols. H_2O; the copper salt of pure β-alanine prepared from β-iodopropionic acid contains $6H_2O$, however.

α-Alanine may accordingly be transformed into the β-compound by first converting it into ethyl acrylate. S. B. A. A.

Derivatives of Angelic and Tiglic Acids. By P. Melikoff and P. Petrenko-Krittchenko (*Annalen*, **257**, 116—132; compare Abstr., 1887, 29, and 1888, 1177).—The authors have made some further experiments in order to show that the α-chloro-α-methylhydroxybutyric acid (m. p. 115·5°) obtained from tiglic acid (Abstr., 1887, 29) is not identical with the α-chlorhydroxyvaleric acid (m. p. 103°, not 105°) obtained by treating angelic acid with hypochlorous acid; this is clearly proved by a comparison of the behaviour of the potassium and silver salts of the two acids, as well as by a comparison of the two acids themselves.

The β-chlorohydroxy-acid (m. p. 92°) obtained by the combination of hydrochloric acid and the glycidic acid from angelic acid is isomeric with the β-chlorhydroxy-acid (m. p. 75°) which is obtained by the action of hypochlorous acid on angelic acid, and on tiglic acid. When the acid (m. p. 92°) is warmed with sodium carbonate, it is converted into ethyl methyl ketone, identical with the compound obtained from the β-chlorhydroxy-acid prepared from tiglic acid; the acid melting at 92° is therefore αβ-chlor-α-hydroxy-, and that melting at 103° an α-chloro-β-hydroxy-valeric acid.

The authors discuss the behaviour of various unsaturated acids with hypochlorous acid, and conclude that Michael's rules (Abstr., 1819, 1140) are inapplicable in a large number of cases.

F. S. K.

Schmidt's Process for the Conversion of Oleic Acid into Solid Fatty Acids. By R. Benedikt (*Monatsh.*, **11**, 71—83).—To investigate the process, a mixture of oleic acid with one-tenth of its weight of zinc chloride was heated at about 185° (if the temperature is allowed to rise above 195°, no solid acids are obtained), until a small quantity of it solidified when cooled. The solid product of the action consisted of additive products with zinc chloride, and these, on boiling with dilute hydrochloric acid, were converted into isomeric hydroxystearic acids, one of which was further converted by loss of water into the lactone of γ-hydroxystearic acid. The action of zinc chloride consequently resembles that of sulphuric acid (compare Geitel, Abstr., 1888, 578), and confirms the opinion of Saytzeff (Abstr., 1888, 815), that oleic acid must be represented by the formula

$$CH_3 \cdot [CH_2]_{13} \cdot CH{:}CH \cdot CH_2 \cdot COOH.$$

On distilling these hydroxystearic acids, oleic and the solid isoleic acids are formed. Schmidt's solid "fatty acids" consist chiefly of a mixture of isoleic acid and stearolactone.

G. T. M.

Ethyl α-β-Diacetopropionate. By I. Ossipoff (*Bull. Soc. Chim.* [3], **3**, 326—328).—Ethyl sodacetoacetate and chloracetone in molecular proportion were heated in alcohol at 100°, and on distillation yielded two fractions, one boiling at 104—106° under a pressure of 37—38 mm., and another boiling at 121—123° under a pressure of 33—35 mm. Neither of these is pure ethyl diacetopropionate, but each contains much ethyl acetoacetate.

The heats of combustion of the second fraction were taken, and gave a mean value of 1110 cals. T. G. N.

Acetyllevulinic Acid and Constitution of γ-Ketone Acids. By J. Bredt (*Annalen*, **256**, 314—340).—Acetyllevulinic acid (Abstr., 1887, 126) is formed when α-angelicalactone is treated with acetic anhydride at the ordinary temperature, or more quickly, at 100°, a reaction which is further evidence in favour of the lactone formula for levulinic acid.

The *hydrazone* of levulinic phenylhydrazide,

$$NHPh \cdot N{:}CMe \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH \cdot NHPh,$$

is formed when acetyllevulinic acid is treated with phenylhydrazine in glacial acetic acid solution, or when α-angelicalactone is treated with phenylhydrazine in ethereal solution; it crystallises from hot alcohol in prisms, and melts at 178°. The formation of this compound cannot be regarded as evidence against the lactone formula for acetyllevulinic acid, because the diacetates of aldehydes behave in an exactly similar manner. When benzaldehyde diacetate, $CHPh(OAc)_2$, for example, is treated with phenylhydrazine in glacial acetic acid solution, the hydrazone of the benzaldehyde separates from the solution in crystals, and the mother liquors contain acetylphenylhydrazine (m. p. 128·5°).

Œnanthaldehyde diacetate, under the same conditions, is converted into œnanthaldehydephenylhydrazine and acetylphenylhydrazine.

The dilactone, $\begin{matrix} CH_2\cdot CH_2 \\ | \qquad \\ CO - O \end{matrix} > C < \begin{matrix} CH_2\cdot CH_2 \\ \qquad | \\ O - CO \end{matrix}$, isolated by Volhard (this vol., p. 30) from the distillation products of succinic acid, and which stands in the same relation to acetyllevulinic acid as the latter does to aldehyde diacetate, also combines with phenylhydrazine in acetic acid solution. The compound obtained crystallises in colourless needles, does not melt at 290°, and is insoluble in alkalis; it has the composition $C_{19}H_{20}N_4O_2$, and is formed from the intermediate product $COOH\cdot CH_2\cdot CH_2\cdot C(N_2HPh)\cdot CH_2\cdot CH_2\cdot CO\cdot NH\cdot NHPh$, by the elimination of 1 mol. H_2O.

Levulinic cyanide and levulinic chloride both interact with phenylhydrazine, the former, however, only very slowly, yielding the hydrazone of levulinic phenylhydrazide (m. p. 178°) described above. Since both the chloride and the cyanide are doubtless γ-substituted-γ-lactones, acetyllevulinic acid has an analogous constitution,

$$CH_2 < \begin{matrix} CH_2- \\ CO\cdot O \end{matrix} > CHMe\cdot OAc.$$

Levulinic chloride can be conveniently prepared by treating levulinic acid with excess of acetic chloride, and cooling the mixture as soon as the reaction commences; the product is then kept under reduced pressure until free from acetic chloride. Michael's statement that acetyllevulinic is formed in this reaction is incorrect.

Ethyl levulinate is not acted on by acetic anhydride even at 160—170°.

When silver levulinate is treated with acetic chloride, or when silver acetate is treated with levulinic chloride, acetyllevulinic acid is formed. F. S. K.

Action of Ammonia on Dehydrodiacetyllevulinic Acid. By G. MAGNANINI (*Gazzetta*, **19**. 275—284).—The formation of dehydrodiacetyllevulinic acid, $C_9H_{10}O_4$, by heating levulinic acid with acetic anhydride was previously described (Abstr., 1888, 812).

The best yield is obtained by heating levulinic acid with acetic anhydride for not less than 10 hours at a temperature of 220—225°, removing the excess of acetic acid and anhydride by distillation in a vacuum, treating the resinous residue with water, and completely

extracting by boiling with sodium carbonate. The alkaline solution is repeatedly extracted with ether, the extract freed from ether, and the residue crystallised from boiling water; the yield never exceeds 4 per cent. By evaporating the ethereal solution, it may be obtained in monoclinic prisms, $a:b:c = 1{\cdot}58975:1:{\cdot}087707$, $\beta = 69° 41' 13''$. Forms observed (001), (100), (010), (110), ($\bar{2}$01), ($\bar{1}$11), (*hko*), (*hol*).

The ethereal extract from the alkaline solution contains an oil having an agreeable odour and boiling at 73—85° under a pressure of 9—10 mm. of mercury.

The action of acetic anhydride on levulinic acid at 100° results in the quantitative conversion of the latter into its monacetyl-derivative. On heating levulinic acid with five times its weight of acetic anhydride for six hours at 150—155°, a mixture of acetyllevulinic acid and of angelolactone is obtained, but no dehydrodiacetyl-levulinic acid is formed if the temperature is either much below 200° or over 230°.

When the acid (1 gram) is heated in a sealed tube with ammonia (12—13 grams, sp. gr. = 0·905) for 5—6 hours at 100°, it is almost quantitatively converted into the compound $C_8H_{11}NO$, which partially separates on standing in long, lustrous needles. The bulk of this product is extracted from the solution with ether, it melts when pure at 94·5°, and has an odour recalling that of an acetylpyrroline. On heating it with zinc-dust, an oil passes over having an odour recalling that of the homologues of pyrroline, and colouring a strip of pinewood moistened with hydrochloric acid an intense red; it is itself resinified by that reagent.

The compound $C_8H_{11}NO$ does not yield an oxime on heating it with hydroxylamine hydrochloride, sodium carbonate, and alcohol, the product consisting of the sodium salt of a new acid which is precipitated by ether from a concentrated alcoholic solution, and decomposes at 162°. S. B. A. A.

Ethereal Salts of Alkyoxyquartenylic Acids. By E. Enke (*Annalen*, **256**, 201—218; compare Koll, Abstr., 1889, 488).—Ethyl β-chloroquartenylate, $CH_2{:}CCl{\cdot}CH_2{\cdot}COOEt$, is obtained by dissolving β-chloroquartenylic acid, prepared by Geuther's method, in alcohol, and saturating the solution with hydrogen chloride; it boils at 155—157°. The *methyl* salt boils at 139—141°, the *propyl* salt at 175—177°, and the *isobutyl* salt at 187°.

Methyl β-methoxyquartenylate, $CH_2{:}C(OMe){\cdot}CH_2{\cdot}COOMe$, obtained by treating methyl chloroquartenylate with sodium methoxide in alcoholic solution, is a colourless liquid boiling at 175·8° (corr.); the corresponding *ethoxy*-derivative boils at 195·7° (corr.), the *propoxy*-derivative at 230·4° (corr.), and the *isobutoxy*-derivative at 253·7° (corr.).

Ethyl β-methoxyquartenylate, $CH_2{:}C(OMe){\cdot}CH_2{\cdot}COOEt$, boils at 178·4° (corr.), the *propoxy*-derivative at 228·6° (corr.), the *isobutoxy*-derivative at 247·3° (corr.), and the *amyloxy*-derivative at about 254—260° with partial decomposition.

Propyl β-methoxyquartenylate boils at 180—182°; the *ethoxy*-deriva-

tive melts at 18° and boils at 205·3° (corr.), the *propoxy*-derivative boils at 229·7° (corr.), and the *isobutoxy*-derivative at 251·4° (corr.).

Butyl β-methoxyquartenylate boils at 184·5° (corr.); the *ethoxy*-derivative melts at 11° and boils at 206·4° (corr.), the *propoxy*-derivative boils at 228·5° (corr.), and the *isobutoxy*-derivative at 249·8° (corr.).

F. S. K.

Action of Sodium and Sodium Ethoxide on Ethereal Salts of Lactone Acids and on Lactones. By R. Fittig (*Annalen*, **256**, 50—63; compare Abstr., 1885, 375).—It has been previously shown (Roser, Abstr., 1884, 459, and Frost, Abstr., 1885, 393) that when ethyl terebate (ethyl dimethylparaconate) is treated with sodium or sodium ethoxide, it is converted into sodium ethyl tereconate; the ethyl salts of propyl-, isobutyl-, and phenyl-paraconic acid behave in like manner, being converted into the sodium ethyl salts of the isomeric itaconic acids in accordance with the equation

$$CO<\begin{matrix}O-CHX \\ CH_2\cdot CH\cdot COOH\end{matrix} = CHX{:}C(COOH)\cdot CH_2\cdot COOH.$$

The same intramolecular change takes place to a slight extent, as has been already shown (compare this vol., pp. 584, 775), when the substituted paraconic acids are distilled; the unsaturated bibasic acids obtained by either of these methods being identical.

Methylitaconic acid, propylitaconic acid, and phenylitaconic acid are readily converted into saturated acids; isobutylitaconic acid, on the other hand, is as difficult to reduce as teraconic acid. In chemical behaviour the itaconic acids resemble teraconic acid very closely, but, unlike the latter, they are only very partially reconverted into the paraconic acids by treatment with hydrochloric, hydrobromic, or sulphuric acid; this change can, however, be brought about by treating the acids with bromine and then with sodium amalgam. By boiling the acids obtained by the action of bromine on propyl- and isobutyl-itaconic acids with water, the unsaturated lactone acids corresponding to aconic and terebilenic acid are formed; the constitution of these compounds is probably expressed by the formula $CO<\begin{matrix}O-CHX \\ CH{:}C\cdot COOH\end{matrix}$.

The brominated phenylparaconic acids behave quite differently, as, when boiled with water, they are decomposed with evolution of carbonic anhydride, yielding benzoylpropionic acid.

The ethyl salt of terpenylic acid shows a totally different behaviour from that exhibited by the ethereal salts of the substituted paraconic acids, and when treated with sodium or sodium ethoxide, it yields the sodium salts of two isomeric diterpylic acids, $C_{16}H_{22}O_7$, 2 mols. of the lactone acid combining together with elimination of 1 mol. of water. The diterpylic acids are readily decomposed by acids with evolution of carbonic anhydride, yielding crystalline, neutral dilactones, $C_{17}H_{22}O_5$, which form salts, $C_{15}H_{24}O_7M'_2$, when boiled with alkalis; on decomposing these salts with hydrochloric acid, the lactone acids, $C_{15}H_{24}O_6$, are obtained, but they are readily reconverted into dilactones. The abnormal behaviour of terpenylic acid seems to show

that it is not a paraconic acid, and it is possible that it has the constitution $CO<\begin{matrix}O - CPr^{\beta}\cdot COOH\\ CH_2\cdot CH_2\end{matrix}$.

The simple lactones, valerolactone and caprolactone, behave in a certain sense like ethyl terpenylate, as, when treated with sodium ethoxide, they yield sodium salts which are decomposed by hydrochloric acid into dilactones, formed from 2 mols. of the lactone with elimination of 1 mol. of water. These dilactones are decomposed on boiling with bases, giving salts from which crystalline monocarboxylic acids (divalonic and dihexonic acids), polymeric with the original lactones, are obtained; these acids are unstable, and, on warming with dilute mineral acids, are decomposed into neutral, very stable compounds (dimethyloxetone and diethyloxetone). The constitution of these compounds has not yet been ascertained. In the case of valerolactone, the first product (divalerolactone) probably has the constitution $\begin{matrix}CH_2\cdot CH_2\\ CHMe\cdot O\end{matrix}>C{:}C<\begin{matrix}CO\cdot O\\ CH_2\cdot CHMe\end{matrix}$, and the monocarboxylic acid (divalonic acid) obtained therefrom the constitution

$$\begin{matrix}CH_2\cdot CH_2\\ CHMe\cdot O\end{matrix}>C{:}C(COOH)\cdot CH_2\cdot CHMe\cdot OH;$$

on warming this acid with dilute mineral acids, carbonic anhydride is evolved, and it may be assumed that the compound

$$\begin{matrix}CH_2\cdot CH_2\\ CHMe\cdot O\end{matrix}>C(OH)\cdot CH_2\cdot CH_2\cdot CHMe\cdot OH$$

is formed as an itermediate product, and then decomposed into dimethyloxetone, $\begin{matrix}CH_2\cdot CH_2\\ CHMe\cdot O\end{matrix}>C<\begin{matrix}CH_2\cdot CH_2\\ O - CHMe\end{matrix}$, with elimination of water.

The oxetone obtained from caprolactone would, in accordance with these views, be a diethyloxetone of the constitution

$$\begin{matrix}CH_2\cdot CH_2\\ CHEt\cdot O\end{matrix}>C<\begin{matrix}CH_2\cdot CH\\ O - CHEt\end{matrix},$$

and divalonic and dihexonic acid would be dimethyl- and diethyloxetonecarboxylic acid respectively. F. S. K.

Valerolactone. By R. FITTIG and H. RASCH (*Annalen*, **256**, 126—134; compare Abstr., 1885, 375, and preceding abstract).—*Divalolactone*, $C_{10}H_{14}O_3$, is obtained when valerolactone (10 grams) is warmed for about 12 hours with a solution of sodium (2·5 grams) in absolute alcohol (25 grams); after distilling off the alcohol, the product is dissolved in cold water, the well-cooled solution acidified with dilute hydrochloric acid, and the precipitated oil extracted with ether. It gradually solidifies to a yellowish, wax-like mass, but it cannot be obtained in crystals as it is so very readily soluble in all ordinary solvents; it seems to distil under the ordinary pressure with slight decomposition, but is only slightly volatile with steam.

Divalonic acid (*dimethyloxetonecarboxylic acid*), $C_{10}H_{16}O_4$, is formed when divalolactone is warmed for a long time with soda: on acidifying the cold solution with hydrochloric acid, the acid is precipitated as an oil, but it soon solidifies. It crystallises from ether in well-defined, colourless, hexagonal plates, melts at 130° with decomposition, and is readily soluble in alcohol, but only very sparingly in ether, chloroform, and cold water. It dissolves in cold alkaline carbonates with evolution of carbonic anhydride, and is precipitated unchanged on the addition of acids; it does not seem to be acted on by sodium amalgam in alkaline solution. The impure acid decomposes spontaneously with evolution of carbonic anhydride, yielding dimethyloxetone, but the pure compound is stable. The *silver* salt, $C_{10}H_{15}O_4Ag$, crystallises from hot water in dark plates. The *barium* salt, $(C_{10}H_{15}O_4)_2Ba$, is amorphous and readily soluble in alcohol and water. The *calcium* salt, $(C_{10}H_{15}O_4)_2Ca$, is also amorphous, but much more sparingly soluble in alcohol and water than the barium salt.

Dimethyloxetone, $C_9H_{16}O_2$, is formed when divalonic acid is boiled with water or dilute mineral acids. It is a colourless, neutral oil with an agreeable, turpentine-like smell, and boils at 169·5° (thermometer entirely in the vapour); its sp. gr. is 0·978 at 0°, and its molecular formula $C_9H_{16}O_2$, as is shown by vapour-density determinations by V. Meyer's method. It is miscible with alcohol, ether, chloroform, &c., in all proportions, and is soluble in 18 parts of water at the ordinary temperature, but it separates again from the aqueous solution on warming or on adding potassium carbonate. It reduces ammoniacal silver nitrate solution in presence of sodinm hydrate, is readily volatile with steam, and is not decomposed by boiling dilute acids or alkalis. It dissolves in a concentrated aqueous solution of sodium hydrogen sulphite, and cannot be extracted from the solution by shaking with ether. When warmed with hydroxylamine in aqueous solution, it yields a readily soluble syrup, and it combines with phenylhydrazine to form a yellowish oil. It is not acted on by acetic anhydride at 190°, or by sodium amalgam, but when heated with hydriodic acid it is completely decomposed.

The compound $C_9H_{16}Br_2O$ separates in crystals when dimethyloxetone is treated with ice-cold concentrated hydrobromic acid. It crystallises from chloroform in long needles, melts at 42°, and is very readily soluble in ether, chloroform, carbon bisulphide, light petroleum, &c., but insoluble in cold water; it is decomposed by boiling water and by alkaline carbonates, being reconverted into dimethyloxetone. F. S. K.

Caprolactone. By R. Fittig and H. Dubois (*Annalen*, **256**, 134—147; compare Fittig, Abstr., 1885, 375, and this vol., p. 866).—*Dihexolactone*, $C_{12}H_{18}O_3$, is obtained by treating caprolactone (10 grams) with a solution of sodium (2 grams) in absolute alcohol; after heating at 100° for 3 to 4 hours, the alcohol is evaporated, the residue dissolved in water, the ice-cold solution acidified with hydrochloric acid, and the precipitated oil immediately extracted with ether; the ethereal solution is evaporated at the ordinary temperature, the residual oil shaken first with soda and then with water, to free it

from caprolactone, then dissolved in alcohol, and the filtered solution evaporated, whereon dihexolactone remains as a colourless, mobile, neutral oil. It boils above 300° with slight decomposition, and is readily soluble in alcohol and ether, but only sparingly in water; it is slightly volatile with steam, and is not decomposed by boiling water, but when heated with dilute mineral acids is quickly converted into diethyloxetone.

Dihexonic acid (*diethyloxetonecarboxylic acid*), $C_{12}H_{20}O_4$, is obtained by dissolving dihexolactone in warm soda, shaking the solution with ether to free it from diethyloxetone, acidifying the well-cooled alkaline solution, and extracting the precipitated oil with alcoholic ether. It crystallises in thick, colourless prisms, melts at 106°, and is readily soluble in alcohol and chloroform, but only sparingly in water and ether; it is not acted on by sodium amalgam, and it dissolves unchanged in cold dilute sodium carbonate, but when treated with warm water or cold dilute acids it is converted into diethyloxetone. The *calcium* salt, $(C_{12}H_{19}O_4)_2Ca$, and the *barium* salt, $(C_{12}H_{19}O_4)_2Ba$, are amorphous, soluble in alcohol and water, and decomposed by carbonic anhydride. The *silver* salt, $C_{12}H_{19}O_4Ag$, is insoluble in cold water, but readily soluble in alcohol, from which it separates in amorphous, cauliflower-like aggregates; it is decomposed by boiling water or when heated alone at 100°. The *sodium* salt, $C_{12}H_{19}O_4Na$, crystallises from alcohol in colourless needles, and is decomposed by boiling water.

Diethyloxetone, $C_{11}H_{20}O_2$, prepared by boiling dihexolactone with a dilute mineral acid, is a colourless, mobile, pleasant-smelling liquid, very sparingly soluble (1 in 380 parts at 15°) in water, but readily in alcohol, ether, chloroform, and most ordinary solvents; the aqueous solution becomes turbid on warming, but clear again on heating to about 80°. It is not decomposed by boiling baryta-water or by concentrated sulphuric acid, and with ammoniacal silver nitrate solution, sodium hydrogen sulphite, sodium amalgam, phenylhydrazine, and acetic acid, it behaves like dimethyloxetone (preceding abstract); it does not combine with hydroxylamine, but with benzoic chloride at 100° it yields a thick, brown oil. When heated with dilute (1 : 2) nitric acid it is gradually oxidised, with evolution of carbonic anhydride, yielding caprolactone and an acid which is most probably propionic acid.

The compound $C_{11}H_{10}Br_2O$ is formed when diethyloxetone, dihexolactone, or dihexonic acid is treated with concentrated hydrobromic acid at 0°. It separates from chloroform in colourless crystals, melts at 35°, and is readily soluble in alcohol, ether, and chloroform, but insoluble in water; when treated with sodium amalgam, or boiled with water or sodium carbonate, it is converted into dimethyloxetone.

F. S. K.

Action of Methylamine on Ethyl Maleate and Fumarate. By G. Körner and A. Menozzi (*Gazzetta*, 19, 422—432; compare Abstr., 1887, 1031—1100).—When ethyl maleate is heated with an alcoholic solution of methylamine at 105—110°, the product consists of a mixture of a crystalline solid and a liquid in varying proportions; if the ethyl maleate (12 grams) is heated for 8—10 hours with an

alcoholic solution of methylamine (50 c.c. of 33 per cent.), the product consists of a mass of needles soaked in the solution of the liquid compound; when a smaller quantity of methylamine solution is used (35 c.c. of 25 per cent.), and the heating is continued for 4—5 hours, the liquid product is more abundant.

Methylsuccinamic (methylaspartic) dimethylamide,

$$NHMe\cdot CO\cdot CH(NHMe)\cdot CH_2\cdot CO\cdot NHMe,$$

is the solid product of the preceding reaction, it is separated from the liquid by diluting the mixture with ether and filtering; when pure, it crystallises from absolute alcohol in long, white needles which are very readily soluble in water, easily soluble in alcohol, but almost insoluble in dry ether. The aqueous and alcoholic solutions are strongly alkaline; on heating, they evolve ammonia, becoming first neutral and finally acid; on boiling with baryta-water, methylamine is evolved and barium methylaspartate is formed.

Methylamidomethylsuccinamic acid (dimethylasparagine),

$$NHMe\cdot CO\cdot CH(NHMe)\cdot CH_2\cdot COOH,$$

is obtained by heating the aqueous solution of the preceding compound for several days; on concentrating the solution, a bye-product is first deposited in scales; on further concentration, the solution is converted into a solid mass, which, after repeated crystallisation from alcohol, forms colourless, shining, anhydrous plates which turn yellow at 215° and melt at 291°. The aqueous solution is feebly acid and optically inactive. It combines with both acids and bases: the *nitrate* forms white prisms which contain 1 mol. H_2O, and decompose on heating to 82—83°; the *copper* salt, $(C_6H_{11}N_2O_3)_2Cu + 2H_2O$, forms blue prisms or warty aggregates very soluble in water. On boiling with baryta-water, dimethylasparagine loses a molecule of methylamine with formation of barium methylaspartate.

The deposit of scales obtained in the preparation of dimethylasparagine crystallises from boiling water in flattened, opaque, white, lustrous needles having the composition $C_6H_{10}N_2O_2$; on boiling this substance with baryta-water, the products are the same as those obtained from dimethylasparagine; hence it is either the methylimide of methylaspartic acid or an isomeride.

Diethyl methylaspartate is the liquid product of the action of methylamine on diethyl maleate. The ethereal solution of the crude product also contains small quantities of a crystalline bye-product and traces of methyl maleate. The diethyl salt is obtained pure by moving the ether and alcohol from this solution, precipitating the bye-product with pure ether, converting the methyl aspartate which remains in solution into the chloride or sulphate, and saponifying with soda. It is a colourless and almost odourless oil, heavier than water, and only very sparingly soluble in it, forming an alkaline solution; it combines with acids forming crystalline salts which are very soluble in water, but when boiled with alkaline hydrates or carbonates it undergoes hydrolysis, yielding salts of methylaspartic acid. When heated at 110° with alcoholic methylamine, the dimethylamide is formed; this dissolves slowly in the cold in aqueous methylamine

with formation of dimethylasparagine; it is converted by aqueous ammonia into monomethylasparagine.

The bye-product crystallises from alcohol in shining needles which melt at 144°, and have the composition $C_6H_{11}NO_3$. It is insoluble in dilute alkalis, and is converted by strong ammonia into a white powder which crystallises from water in shining needles; it probably has the constitution $\begin{matrix} CO-CH_2 \\ | \quad\quad | \\ NMe\cdot CH\cdot COOEt \end{matrix}$.

Methylamidosuccinamic acid (*monomethylasparagine*), $C_5H_{10}N_2O_3 + H_2O$, is prepared by heating diethyl methylaspartate with aqueous ammonia until the solution becomes acid; on concentration, a bye-product first crystallises out in scales; subsequently monomethy-asparagine is deposited in spherical aggregates of needles. It combines with both acids and bases. The *copper* salt crystallises in anhydrous bluish-violet scales which decompose at 191°.

On boiling the acid with potash, a methylaspartate is formed with evolution of ammonia; the same reaction takes place on heating with hot mineral acids. Its constitution is therefore expressed by the formula $NH_2\cdot CO\cdot CH(NHMe)\cdot CH_2\cdot COOH$.

The bye-product is probably the imide of methylaspartic acid; it has the composition $C_5H_8N_2O_2$. It crystallises from boiling water in lustrous needles which blacken and decompose at 235°. On boiling with potash or baryta-water, a methylaspartate is formed with evolution of ammonia.

Methylaspartic acid, $C_5H_9O_4 + H_2O$, may be obtained by any of the reactions given. It is best prepared by boiling pure dimethyl-asparagine with baryta-water until no more methylamine is evolved, decomposing the barium salt, and concentrating. It crystallises from boiling water in pointed pyramids which lose their water of crystallisation at 100°, undergo alteration at 120°, and melt at 133—134°. The anhydrous acid melts at 178°. It is sparingly soluble in water (2·62 per cent. in water at 20·4°), and the solution is strongly acid and inactive to light. On standing, it deposits monoclinic, transparent crystals, $a : b : c = 0·6467 : 1 : 0·4489$, $\beta = 80° 25'$. It forms salts with both acids and bases; the *mono-potassium salt* crystallises in shining needles, the *monosodium salt* in nodules, the *monobarium salt* in spherical aggregates of needles containing 4 mols. H_2O; all these salts are very soluble in water, and are precipitated from their solutions by concentrated alcohol in the form of oils. The *ammonium salt* is decomposed by exposure to the air. A *silver salt* is obtained on adding silver nitrate to a solution of an alkaline salt; it is crystalline, and darkens on exposure to light. A crystalline *cadmium salt* may be obtained in the same way. The *nitrate* forms monoclinic tables; the *hydrochloride* crystallises in prisms. The *monethyl salt* is obtained by saturating an alcoholic solution of the acid with hydrogen chloride, and decomposing the hydrochloride with silver oxide and water. It crystallises from 98 per cent. alcohol in very slender, shining needles which melt at 181·5°.

Ethyl fumarate, on treatment with methylamine, yields the same products in the same proportions as ethyl maleate. S. B. A. A.

Eulyte.—By G. CIAMICIAN and C. ZATTI (*Gazzetta*, **19**, 263—267). —Baup (*Annalen*, **81**, 96) and Bassett (this Journal, 1872, 98) described two substances formed by the action of nitric acid on citraconic acid, namely, *eulyte*, $C_6H_6N_4O_7$, and *dislyte*, $C_8H_6N_4O_6$. The directions given by these authors only lead, however, to the formation of *eulyte*. It is best prepared by dissolving pure citraconic acid in nitric acid (sp. gr. = 1·45) and heating until chemical action commences. When the reaction is complete, the product is allowed to remain for some time, and the thick, white, crystalline deposit which forms is filtered through glass fibre; the filtrate yields a further deposit of the white compound on standing. After washing with cold water and drying in a vacuum, this substance melts at 185°, in this respect approximating to dislyte (m. p. = 189°). It consists, however, of a mixture of two substances, as by repeated crystallisation from alcohol its melting point is reduced to 102—102·5°, and by repeatedly dissolving it in ethyl acetate and precipitating with light petroleum an acid compound is obtained melting at 201—202·5°, and identical with mesaconic acid. The same separation may be effected by treating the white deposit with sodium carbonate; the eulyte remains undissolved, and is purified by solution in benzene and reprecipitation with light petroleum. It forms colourless needles which melt at 101—102·5°, and dissolve readily in warm alcohol, benzene, and ethyl acetate. It is almost insoluble in water and in light petroleum, and quite insoluble in cold alkalis, and in acids; it may be heated with concentrated sulphuric acid without undergoing any change. It dissolves in hot potash forming a yellow solution. On treatment with water, the acid filtrate from the eulyte yields an oily substance which still contains eulyte, and spontaneously solidifies after a time. It would appear that maleïc acid is not acted on by nitric acid in a manner analogous to citraconic acid. S. B. A. A.

Ethyl Propylparaconate. By R. FITTIG and A. SCHMIDT (*Annalen*, **256**, 105—109.—*Ethyl propylparaconate*, $C_{10}H_{16}O_4$, is a colourless liquid boiling at 211—216 (96 mm.).

Propylitaconic acid, identical with the compound obtained by distilling propylparaconic acid (this vol., p. 588), is formed when ethyl propylparaconate is treated with sodium ethoxide in absolute alcoholic solution, and the sodium ethyl salt thus produced is hydrolysed with soda; it is not acted on by cold concentrated hydrobromic acid.

Butylsuccinic acid, $C_8H_{14}O_4$, is obtained, together with a volatile compound with a peculiar odour, when propylitaconic acid is treated with sodium amalgam in slightly acid solution. It separates from water in ill-defined crystals and melts at 81°.

When propylitaconic acid is treated with bromine in ice-cold aqueous solution, it yields a crystalline acid melting at 124—124·5°, and an oil with a most irritating odour; the two products are separated by distilling with steam. The acid (m. p. 124—124·5°), which separates from hot water in slender needles, is very readily soluble in chloroform and water, and easily in ether, alcohol, and hot benzene, but is insoluble in carbon bisulphide and light petroleum.

The *barium* salt has the composition $(C_8H_9O_4)Ba$, so that the acid is probably propaconic acid, $CO<\begin{matrix}CH:C\cdot COOH\\ \quad | \\ O—CHPr\end{matrix}$. F. S. K.

Ethyl Terpenylate. By R. FITTIG and S. LEVY (*Annalen*, **256**, 109—126).—*Ethyl terpenylate*, $C_{10}H_{16}O_4$, is obtained by dissolving terpenylic acid, prepared by the method previously described (Fittig and Kraft, Abstr., 1882, 42), in alcohol, and saturating the solution with hydrogen chloride. It forms large, monosymmetric crystals, $a : b : c = 1.0512 : 1 : 0.3805$, $\beta = 50° 58'$, melts at 37·5°, and boils at 305° (thermometer almost entirely in the vapour); it is readily soluble in alcohol and ether, but only sparingly in boiling water.

α- and β-Diterpodilactone are formed when ethyl terpenylate (20 grams) is added to sodium (4 grams) covered with a little pure ether, the mixture heated gradually until the ether has evaporated, and then kept at about 100° for 6 hours. The thick, gum-like product is exposed to the air until the unchanged sodium is completely oxidised, then dissolved in water and any unchanged ethyl terpenylate extracted with ether; the alkaline solution is acidified with hydrochloric acid, the precipitated oil redissolved by diluting and boiling, and the filtered solution allowed to cool, whereon the two dilactones separate in yellowish crystals. The crystalline mixture is boiled with baryta-water, the excess of barium precipitated with carbonic anhydride, and the filtered solution allowed to cool; the barium salt of α-diterpoxylic acid then separates from the solution in well-defined, prismatic crystals, and the mother liquors, on evaporation, yield crystals of the barium salt of the corresponding β-acid.

Barium α-diterpoxylate, $C_{15}H_{24}O_7Ba + 6H_2O$, forms monosymmetric crystals, $a : b : c = 0.9346 : 1 : 0.5949$, $\beta = 65° 54'$, and is readily soluble in hot, but only sparingly in cold water. The *calcium* salt ($+ 6H_2O$), prepared by boiling an aqueous solution of α-diterpodilactone (see below) with calcium carbonate, crystallises from concentrated solutions in colourless, slender needles, and is more readily soluble than the barium salt. The *silver* salt, $C_{15}H_{24}O_7Ag_2$, is insoluble in water. The free *diterpoxylic* acid cannot be isolated.

α-Diterpolactonic acid, $C_{15}H_{24}O_6$, is obtained when an ice-cold solution of barium α-diterpoxylate is carefully treated with dilute hydrochloric acid, and the lactone acid immediately extracted with ether. It separates from cold chloroform in compact, colourless crystals, and is readily soluble in ether and alcohol; it melts at 158—160°, and is decomposed at a somewhat higher temperature with liberation of water and formation of α-diterpodilactone.

α-Diterpodilactone, $C_{15}H_{22}O_5$, is best prepared by boiling an aqueous solution of barium diterpoxylate for a short time with excess of hydrochloric acid; on cooling, the dilactone separates from the solution in colourless needles. It melts at 153—154°, and is almost insoluble in chloroform, benzene, and carbon bisulphide, and only sparingly in cold water, but more readily in alcohol. It is insoluble in cold sodium carbonate, but when boiled with baryta-water, it is gradually converted into barium diterpoxylate.

β-Diterpolactone acid, $C_{15}H_{24}O_6$, separates in crystals when the

mother-liquors from the barium α-diterpoxylate (see above) are treated with cold dilute hydrochloric acid. It separates from water in rhombic prisms, $a : b : c = 0.7319 : 1 : 0.2592$, melts at 186—187°, and decomposes at a slightly higher temperature; it dissolves in sodium carbonate, but is precipitated unchanged on the addition of acids.

Barium β-diterpoxylate ($+ 3\frac{1}{2}H_2O$), prepared by boiling the lactone acid with baryta-water, crystallises in small, colourless needles, and is very readily soluble in water. The *calcium* salt, $C_{15}H_{24}O_7Ca$, is a colourless, semi-crystalline compound, very readily soluble in water. The *silver* salt, $C_{15}H_{24}O_7Ag_2$, is amorphous and only sparingly soluble in water.

β-Diterpodilactone, $C_{15}H_{22}O_5$, prepared by heating the lactone acid above its melting point, or by boiling a solution of barium β-diterpoxylate with dilute hydrochloric acid, crystallises in large, colourless needles, melts at 134—135°, and resembles the corresponding α-compound in its behaviour with solvents; when boiled with baryta-water, it is converted into the barium salt of β-diterpoxylic acid.

α-Diterpylic acid, $C_{16}H_{22}O_7$, is obtained when the alkaline solution of the crude product of the action of sodium on ethyl terpenylate is carefully acidified in the cold with dilute hydrochloric acid, and the precipitated oil immediately extracted with ether; on evaporating the ethereal extract at the ordinary temperature, α-diterpylic acid gradually separates in crystals, whilst the corresponding β-acid remains as an oil. It crystallises from hot water in colourless needles, melts at 216° with decomposition, and is moderately easily soluble in boiling water and hot alcohol, but only sparingly in ether, and almost insoluble in cold water. The *barium* salt crystallises in small needles and is readily soluble in water; the *calcium* salt crystallises in plates and is only sparingly soluble. When the acid is heated for a long time at 216°, or boiled with dilute hydrochloric acid, it is completely converted into α-diterpodilactone. F. S. K.

Ethyl Isobutylparaconate. By R. FITTIG and J. KRAENCKER (*Annalen*, **256**, 97—105).—*Ethyl isobutylparaconate*, $C_{11}H_{18}O_4$, is obtained by saturating an alcoholic solution of the acid, prepared as previously described (this vol., p. 590), with hydrogen chloride; it is a colourless, crystalline compound, melts at 16—17°, and boils at 293°.

Isobutylitaconic acid, $COOH{\cdot}CH_2{\cdot}C(COOH){:}CH{\cdot}CH_2Pr^{\beta}$, is prepared by treating ethyl isobutylparaconate with sodium ethoxide in alcoholic solution and hydrolysing the product with soda as described in the preparation of phenylitaconic acid (this vol., p. 895); small quantities of succinic acid and regenerated isobutylparaconic acid are also formed in the reaction, and the itaconic acid is best obtained in a pure condition by dissolving the acid mixture in water, neutralising with calcium carbonate and boiling the filtered solution, whereon calcium isobutylitaconate separates as a powder. The acid separates from water in ill-defined crystals, and melts at 160—165° with liberation of water; when heated quickly, the temperature may be raised to 170° before the acid is completely liquefied. It is rather sparingly soluble in chloroform, benzene, and hot water, but readily in alcohol and ether. The *calcium* salt, $C_9H_{12}O_4Ca$, and the *barium* salt,

$C_9H_{12}O_4Ba$, are more readily soluble in cold than in hot water. The *silver* salt, $C_9H_{12}O_4Ag_2$, is very sparingly soluble in hot water, and gradually darkens on exposure to the light. The *ethyl* salt, $C_9H_{12}O_4Et_2$, is a colourless liquid, and boils at 268°. Isobutylitaconic acid is not reduced by sodium amalgam, and when heated with concentrated hydrochloric or sulphuric acid, only a trace of isobutylparaconic acid is formed, most of the acid remaining unchanged.

Isobutaconic acid, $CO<\begin{matrix}O—CH\cdot CH_2Pr^{\beta}\\ \quad | \\ CH:C\cdot COOH\end{matrix}$, is obtained, together with a neutral oil, the nature of which could not be ascertained, when isobutylitaconic acid is suspended in water and treated with bromine; the neutral oil, which contains bromine, is separated by distilling with steam, the residual solution extracted with ether, and the mixture of isobutaconic acid and isobutylitaconic acid obtained in this way separated into its constituents by means of their calcium salts. Isobutaconic acid crystallises from water in long, colourless needles, and melts at 165—170° with partial decomposition. The *calcium* salt, $(C_9H_{11}O_4)_2Ca$, and the *barium* salt, are crystalline compounds, readily soluble in water and alcohol. The *silver* salt, $C_9H_{11}O_4Ag$, is only sparingly soluble in water. When the acid is reduced with sodium amalgam, it is converted into isobutylparaconic acid. F. S. K.

Reduction-products of Dichloromuconic Acid. By A. BAEYER and H. RUPE (*Annalen*, **256**, 1—28; compare Baeyer, Abstr., 1888, 1069, and 1889, 1176).—The remarkable reduction of $\Delta^{1,3}$-dihydroterephthalic acid to Δ^2-tetrahydroterephthalic acid led the authors to investigate the behaviour of dichloromuconic acid. From the results of this investigation, Baeyer concluded that the double linkings in the unsaturated hydroterephthalic acids behave exactly like those of open chain unsaturated fatty acids, provided it be assumed that the presence of halogen-atoms does not influence the course of the reactions. The behaviour of mucic acid itself has now been studied; the results show the complete analogy between this acid and $\Delta^{1,3}$-dihydroterephthalic acid, and prove the correctness of Baeyer's conclusion.

The dichloromuconic acid, $COOH\cdot CH:CCl\cdot CCl:CH\cdot COOH$, employed in these experiments was prepared by Bode's method (*Annalen*, **132**, 95); the *methyl*-salt, obtained by treating the acid chloride with methyl alcohol in the cold, crystallises from hot dilute alcohol in colourless, nacreous plates, melts at 156°, and is readily soluble in ether, hot alcohol, and glacial acetic acid.

$\Delta^{\beta\gamma}$-Hydromuconic acid, $COOH\cdot CH_2\cdot CH:CH\cdot CH_2\cdot COOH$, can be obtained by dissolving dichloromuconic acid (5 grams) and sodium hydroxide (12 grams) in water (50 grams), and gradually treating the ice-cold solution with 4 per cent. sodium amalgam (60 to 80 grams), the whole being constantly shaken; if the solution is not shaken well, 120 to 140 grams of the amalgam are required. The solution is then decanted from the mercury, nearly neutralised with dilute sulphuric acid in the cold, the filtered solution carefully neutralised and evaporated until crystallisation commences; the sodium sulphate

is separated by filtration, the hydromuconic acid precipitated with dilute hydrochloric acid, and, after keeping for 12 hours, separated by filtration, washed with a little water, and recrystallised from hot water. It forms long, colourless, pointed prisms, melts at 195°, and is identical with Bode's "muconic acid" (*loc. cit.*). The constitutional formula $COOH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, previously assigned to this acid by Baeyer, who obtained it by reducing diacetylenedicarboxylic acid (Abstr., 1885, 760), is incorrect. It is only sparingly soluble (1 in 170 parts at 15°) in water, and when boiled with soda, it is converted into the isomeric $\Delta^{\alpha\beta}$-acid, so that it must be regarded as the labile form of hydromuconic acid. The calcium, barium, and strontium salts are more sparingly soluble in cold than in hot water. The *methyl* salt is formed when methyl dichloromuconate is treated with zinc-dust and glacial acetic acid; as soon as the addition of zinc-dust produces no further development of heat, the solution is filtered, the filtrate treated with sodium carbonate until a permanent precipitation is produced, and then extracted with ether. It is a yellowish, rather mobile oil, which solidifies in a freezing mixture; on hydrolysis with cold dilute soda, it yields hydromuconic acid (m. p. 195°). When $\Delta^{\beta\gamma}$-hydromuconic acid is oxidised with 3 per cent. potassium permanganate in the cold, it yields malonic acid, a proof that it has the constitution assigned to it above.

$\Delta^{\alpha\beta}$-*Hydromuconic acid*, $COOH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, is formed when the labile modification (m. p. 195°) is boiled with excess of soda; as soon as a crystalline precipitate is produced, the solution is diluted, acidified with dilute sulphuric acid, and kept for a long time, whereon crystals of the new acid separate from the solution. It crystallises from hot water in plates, melts at 168—169°, and is moderately easily soluble (1 in 111 parts) in cold water, but only sparingly in ether. Its salts do not differ appreciably from those of the labile acid. On oxidation with 3 per cent. potassium permanganate, it yields oxalic acid and succinic acid.

Both muconic acid and the hydromuconic acids can, theoretically, exist in geometrically isomeric modifications; electrolytic measurements carried out by Ostwald seem to show that the stable hydromuconic acid is a mixture.

Adipic acid can be obtained by reducing dichloromuconic acid with sodium amalgam in boiling alkaline solution, but the process is rather troublesome.

Methyl β-bromhydromuconate is obtained when β-bromo-$\Delta^{\beta\gamma}$-hydromuconic acid, $COOH{\cdot}CH_2{\cdot}CBr{:}CH{\cdot}CH_2{\cdot}COOH$ (m. p. 183°), prepared by treating $\Delta^{\beta\gamma}$-hydromuconic acid with bromine in hot aqueous solution, is converted into the acid chloride, and then treated with methyl alcohol in the cold; it crystallises from hot alcohol in long, colourless needles melting at 80°.

A *bromhydromuconic acid* is obtained when a hot concentrated solution of $\Delta^{\alpha\beta}$-hydromuconic acid is treated with bromine until a permanent coloration is produced. In crystallises in very slender needles, melts at 158—160°, and has probably the constitution

$$COOH{\cdot}CBr{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH.$$

$\beta\gamma$-Dibromadipic acid (m. p. 190°) is formed when $\Delta^{\beta\gamma}$-hydromuconic acid is treated with bromine; if large quantities of the acid are employed the yield is very small. It crystallises in colourless needles, and is identical with the acid obtained by Limpricht by brominating $\Delta^{\beta\gamma}$-hydromuconic acid in hot acetic acid solution. The *methyl* salt, $C_8H_{12}Br_2O_4$, prepared by brominating methyl hydromuconate in chloroform solution, crystallises in long needles, and melts at 78°.

The acid (m. p. 205°) obtained by Ador (*Ber.*, **4**, 627) by treating hydromuconic acid with bromine in aqueous solution is identical with $\beta\gamma$-dibromadipic acid (m. p. 190°).

Attempts to prepare the bromo-additive compound of $\Delta^{\alpha\beta}$-hydromuconic acid were unsuccessful, but the *methyl* salt, $C_8H_{12}Br_2O_4$, can be obtained by treating methyl $\Delta^{\alpha\beta}$-hydromuconate with bromine in chloroform solution; it crystallises in small needles, and melts at 84—85°.

Muconic acid, COOH·CH:CH·CH:CH·COOH, can be prepared by dissolving $\Delta^{\beta\gamma}$-dibromadipic acid in hot alcohol, adding to the cold solution a little more than the theoretical quantity of 22 per cent. alcoholic potash, and then boiling for five to seven minutes. The precipitated potassium salt and the potassium bromide are separated by filtration, washed with absolute alcohol, dried on a porous plate, then dissolved in water, and the muconic acid precipitated with sulphuric acid; the yield is 85 per cent. of the theoretical. It crystallises in very small, moss-like needles, turns brown at about 250°, and does not melt below 260°; it is very sparingly soluble (1 in 5000) in cold, but rather more readily in hot water, and moderately easily in hot alcohol and hot glacial acetic acid. It is immediately oxidised and completely destroyed by potassium permanganate. The *silver* salt, $C_6H_4O_4Ag_2$, is a colourless, amorphous compound, moderately stable in the light. The *copper* salt is a bluish-green, sparingly soluble, amorphous compound. The *calcium*, *barium*, and *strontium* salts are more sparingly soluble in hot than in cold water. The *methyl* salt, $C_8H_{10}O_4$, prepared from the chloride, crystallises from hot alcohol in slender needles, and melts at 154°; when treated with sodium amalgam in ice-cold alkaline solution, it is converted into $\Delta^{\beta\gamma}$-hydromuconic acid (m. p. 195°). The "muconic" acid obtained by Limpricht by treating $\beta\gamma$-dibromadipic acid with silver oxide is a monobasic acid, and has probably the constitution

$$\begin{array}{l}CH_2{\cdot}CH \\ | \\ CO - O\end{array}\!\!>C{\cdot}CH_2{\cdot}COOH.$$

Tetrabromadipic acid, $C_6H_4Br_4O_4$, is obtained when finely divided muconic acid is treated with bromine. It crystallises from hot dilute alcohol in small plates, begins to turns brown at 230°, and decomposes completely at 250°; it is sparingly solnble in hot water, but moderately easily in hot dilute alcohol, glacial acetic acid, and ether. The *methyl* salt, $C_8H_{10}Br_4O_4$, prepared from the acid chloride, crystallises in colourless needles melting at 74°. F. S. K.

Synthesis of Diakyl-substituted Glutaric Acids and of Compounds containing closed Carbon Chains. By M. Guthzeit

and O. Dressel (*Annalen*, **256**, 171—201).—Ethyl dicarboxyglutarate, prepared by the method previously described (Abstr., 1888, 1061), boils at 192° under a pressure of 12 mm., and at 300—310° under the ordinary pressure with partial decomposition; when hydrolysed with moderately concentrated (1 : 1) sulphuric acid, it is converted into glutaric acid, the yield being nearly theoretical.

A monosodium-derivative of ethyl dicarboxyglutarate could not be obtained; the disodium-derivative has been prepared by Perkin (Abstr., 1886, 691).

Ethyl dimethyldicarboxyglutarate,

$$(COOEt)_2CMe\cdot CH_2\cdot CMe(COOEt)_2,$$

is obtained when ethyl dicarboxyglutarate (1 mol.) is treated with sodium (1 mol.) and methyl iodide (2 mols.) in alcoholic solution, and the mixture warmed, if necessary, until the solution is neutral. It is a colourless oil, and boils at 191° (12 mm. pressure). The free *acid* $C_9H_{12}O_8$, prepared by hydrolysing the ethereal salt with alcoholic potash, is a colourless crystalline compound, melts at 164° with evolution of carbonic anhydride when heated quickly, and is readily soluble in water, but more sparingly in ether; it is decomposed by boiling water. In aqueous solutions of the ammonium salt, the chlorides of barium, strontium, and mercury, and silver nitrate, produce colourless precipitates, but salts of calcium and many other metals produce no precipitation.

Dimethylglutaric acid, $CH_2(CHMe\cdot COOH)_2$, prepared by hydrolysing ethyl dimethyldicarboxyglutarate with sulphuric acid, separates from ether in crystals, melts at about 90°, and is readily soluble in water, alcohol, and ether; in aqueous solutions of the ammonium salt, silver nitrate and mercuric chloride produce colourless precipitates, but salts of the alkaline earths and many metals give no precipitate.

Ethyl diethyldicarboxyglutarate, $C_{19}H_{32}O_8$, crystallises in large, well-defined prisms, melts at 61°, boils at 195° (12 mm.), and is very readily soluble in all ordinary solvents. The free *acid* $C_{11}H_{16}O_8$, obtained by boiling the ethereal salt for a long time with absolute alcoholic potash, is a colourless, crystalline compound melting at 163° with evolution of carbonic anhydride. In aqueous solutions of the ammonium salt, silver, mercury, lead, and iron salts produce precipitates, but the salts of the alkaline earths, and of zinc, nickel, and cobalt, are readily soluble.

Diethylglutaric acid, $C_9H_{16}O_4$, is crystalline, melts at about 63°, and is readily soluble in ether, but only sparingly in water; in aqueous solutions of the ammonium salt, silver nitrate, mercuric chloride, or lead acetate produce a colourless, and ferric chloride a brown, precipitate; the other metallic salts are readily soluble.

Attempts to prepare the monethyl-derivative of ethyl dicarboxyglutarate described by Kleber (Abstr., 1888, 1056) were unsuccessful; Kleber's compound is most probably a mixture of ethyl dicarboxyglutarate and the diethyl-derivative.

Ethyl dipropyldicarboxyglutarate, $C_{21}H_{36}O_8$, forms large crystals, melts at 42°, boils at 207—208° (12 mm.), and is readily soluble in

all ordinary solvents. The free *acid*, $C_{13}H_{20}O_8$, melts at 167, with decomposition, and resembles diethyl dicarboxyglutarate very closely, except that it is more sparingly soluble in water.

Dipropylglutaric acid, $C_{11}H_{20}O_4$, crystallises from ether, melts at about 89°, and is very sparingly soluble in water. In neutral aqueous solutions, silver, mercury, lead, and zinc salts produce a colourless, copper salts a blue, and ferric chloride a yellow, precipitate; the salts of the alkaline earths are readily soluble.

Ethyl diallyldicarboxyglutarate, $C_{21}H_{32}O_8$, melts at 30—31°, and boils at 213—215° (20 mm.). *Ethyl dibenzyldicarboxyglutarate*, $C_{29}H_{36}O_8$, is a thick oil.

Ethyl trimethylenetetracarboxylate (1, 1, 2, 2,), prepared by the method described by Perkin (*loc. cit.*), crystallises in long needles, melts at 43°, boils at 187° (12 mm.), and is readily soluble in all ordinary solvents. The free *acid*, $C_7H_6O_8$, separates from cold water in large crystals, decomposes at about 200°, and is not acted on by potassium permanganate in cold alkaline solution; in concentrated aqueous solutions of the ammonium salt, precipitates are produced by salts of lead, silver, and the alkaline earths. When the acid is heated at 200—230°, and then distilled under reduced pressure (15 mm.), the anhydride of trimethylenedicarboxylic acid passes over between 170° and 180°, and quickly solidifies on cooling (compare Conrad and Guthzeit, Abstr., 1884, 991).

Ethyl tetramethylenetetracarboxylate, $C_{16}H_{14}O_8$ (1, 1, 3, 3,), is obtained when ethyl disodiodicarboxyglutarate is treated with methylene iodide in alcoholic solution; it is a thick oil boiling at 220—250° (15 mm.) with partial decomposition; on hydrolysis with alcoholic potash, it yields a small quantity of an acid melting at 115°, probably impure tetramethyleuedicarboxylic acid. F. S. K.

Action of Ammonia on Lactones. By R. FITTIG (*Annalen*, **256**, 147—149; compare Abstr., 1884, 744).—Lactones combine with ammonia in alcoholic or aqueous solution yielding the amide of the corresponding γ-hydroxy-acid; the ammonium salt of the hydroxy-acid is not formed under any conditions. The presence of water is necessary in order that the reaction may take place at the ordinary temperature; when an absolute alcoholic solution of ammonia is employed, combination takes place only very slowly even at 100°.

The amides of the γ-hydroxy-acids are very unstable; they are decomposed by dilute acids or dilute alkalis at the ordinary temperature, and also when heated alone at a moderately high temperature (158—200°), yielding ammonia and the lactone. F. S. K.

γ-Hydroxyvaleramide. By R. FITTIG and H. RASCH (*Annalen*, **256**, 149—152; compare Neugebauer, Abstr., 1885, 65, and Fittig, preceding abstract).—γ-Hydroxyvaleramide, $C_5H_{11}O_2N$, is a colourless, hygroscopic compound, very readily soluble in water and alcohol, but only sparingly in chloroform and ether; on the addition of ether to a concentrated alcoholic solution, it is precipitated in plates melting at 56°.

Ammonium γ-hydroxyvalerate, $C_5H_{13}O_3N$, prepared by treating a solution of barium hydroxyvalerate with ammonium sulphate, crystallises in stellar aggregates, and is more sparingly soluble in water

than the amide; it decomposes at 115° yielding ammonia, water, and valerolactone. F. S. K.

γ-Hydroxycapronamide. By R. FITTIG and H. DUBOIS (*Annalen*, **256**, 152—155; compare Fittig, this vol., p. 879).—*γ-Hydroxycapronamide*, $OH·CHEt·CH_2·CH_2·CO·NH_2$, separates from chloroform in colourless, prismatic crystals, melts at 74°, and is very readily soluble in water and alcohol.

Ammonium γ-hydroxycaproate, $C_6H_{15}O_3N$, prepared from the barium salt, separates from alcohol in hygroscopic crystals, and melts at 90° with decomposition; at 100° it is converted into water, ammonia, and caprolactone. F. S. K.

ψ-Selenocarbamides. By W. BARINGER (*Ber.*, **23**, 1003—1006; compare preceding abstract).—On heating potassium selenocyanate with bromethylamine hydrobromide, and extracting the residue with alcohol, *ethylene-ψ-selenocarbamide hydrobromide*,

$$\begin{matrix}CH_2—Se\\|\\CH_2·NH\end{matrix}\!\!>C:NH,HBr,$$

crystallises out in needles which melt at 170°. The free base is an unstable, oily liquid. The picrate crystallises from water in needles melting at 220°. The platinochloride is obtained in the form of light yellow, cubical crystals which are easily soluble in water. *Trimethylene-ψ-selenocarbamide hydrobromide*,

$$CH_2<\begin{matrix}CH_2—Se\\CH_2·NH\end{matrix}>C:NH,HBr,$$

is obtained in a similar manner by the action of potassium selenocyanate on γ-bromopropylamine hydrobromide; it crystallises from alcohol in white needles which melt at 133—135° The picrate is easily soluble in water, from which it is deposited in the form of concentric needles melting at 50—53°. β-Bromopropylamine and potassium selenocyanate yield *propylene-ψ-selenocarbamide hydrobromide*, $\begin{matrix}CHMe·Se\\|\\CH_2·NH\end{matrix}\!\!>C:NH,HBr$. The picrate crystallises from water in interlaced needles melting at 110°. The corresponding ψ-carbamides are obtained by the oxidation of these bases with bromine-water, the selenium being replaced by oxygen. J. B. T.

Sulphines. By G. PATEIN (*Bull. Soc. Chim.* [3], **3**, 164—171; compare Abstr., 1889, 234).—The following double salts, which exist as crystalline, deliquescent masses, are described:—

$SMe_3·CN,AgCN$, melting at 145—146°;
$SEt_3·CN,AgCN$, melting at 25—26°;
$SMe_2Et·CN,AgCN$, melting at 78—79°; and
$SMeEt_2·CN,AgCN$, melting at 45—46°.

The author endeavoured to prepare from these double cyanides the corresponding sulphine cyanides, and in the case of the substance $SMe_3·CN,AgCN$, found that potassium cyanide reacted therewith to form ammonia and methyl sulphide; hydrogen sulphide generated a sulphine thiocyanate, and acetonitrile, when heated with the double

salt in sealed tubes at 120° for several hours, caused the formation of methyl sulphide. The following method succeeded:—Trimethylsulphine iodide is treated with a sufficient quantity of moist silver oxide to form trimethylsulphine hydroxide, which is taken up with water, evaporated to a syrup, and treated with alcohol; to the filtered alcoholic liquid, a strong aqueous solution of hydrocyanic acid is added, and it is then evaporated in a vacuum, yielding a crystalline mass, which, after being dissolved in alcohol, is purified by precipitation with ether, and subsequent evaporation in a vacuum. The crystals of trimethylsulphine cyanide thus obtained are small, colourless, deliquescent cubes which are soluble in water and alcohol, but are insoluble in ether; with dilute acids they yield the corresponding salts of the sulphine, and with silver iodide and cyanide form the double salts previously described; when treated with aqueous potash at 160°, it yields methyl sulphide and methylamine.

The crystalline double salt, $SMe_2,ZnBr_2$, is further described; it yields with mercuric chloride a compound $SMe_2,HgBrCl$, and precipitation of the zinc by reagents sets free methyl sulphide.

The derivative SMe_2Br_2, when heated in sealed tubes at 100° for several hours with alcohol and silver acetate, yields methyl sulphide and trimethylsulphine bromide and acetate.

Trimethylsulphine iodide and triethylsulphine iodide, when heated in sealed tubes at 100° for 12 hours with sodium ethoxide, yield respectively methyl and ethyl sulphides.

When the sulphine iodides are heated with alcoholic ammonia in sealed tubes for some hours, the corresponding alkyl sulphides are obtained, together with an amine.

The product of the reaction between ethyl sulphide (1 mol.) and bromine (1 mol.), after saturation with aqueous ammonia and distillation, yields an oily liquid which passes over with the ammoniacal distillate, and crystallises on cooling; after extraction of this substance with ether, evaporation of the solvent, and subsequent sublimation of the residue, a small amount of light, white crystals of the formula $C_7H_{16}N_2S$ (?) are obtained. These melt at 73—74°, are insoluble in water, but soluble in alcohol and in ether. They form soluble salts with acids and an unstable crystalline aurochloride.

T. G. N.

Benzene Formulæ. By A. LADENBURG (*Ber.*, **23**, 1007—1011).—This is a reply to part of Baeyer's address at the Kekulé festival. Whilst admitting that the formation of naphthalene, &c., is best represented by Kekulé's formula, the author is of opinion that the relations between terephthalic and succinic acids on the one hand, and between phthalic and adipic acids on the other, are much more clearly shown by the "prism formula" than by Kekulé's hexagonal formula with double bonds.

J. B. T.

Metamerism in Derivatives of Benzene. By A. HAND (*Annalen*, **256**, 264—268).—The "second" monobromobenzene, described by Fittica (*Ber.*, **18**, 2634), is simply a mixture of benzene and ethyl bromide.

F. S. K.

New Method of Chlorinating Aromatic Compounds. By PÉTRICOU (*Bull. Soc. Chim.* [3], **3**, 189—191).—Benzene (400 c.c.) and granulated tin (90 grams) were placed in a reflux apparatus, and chlorine was passed in for 20 hours, when more tin (150 grams) was added, and the current of chlorine continued for 90 hours. During the reaction much hydrogen chloride was evolved. The resulting solid mass, after washing and drying, was fractionated, and yielded 562 grams of chlorobenzenes fractionating at temperatures between 244—277°, and some hexachlorobenzene.

A second experiment, in which chlorine was passed into a mixture of benzene (400 c.c.) and tin (100 grams) for 36 hours, yielded 142 grams of 1 : 4-dichlorobenzene, 114 grams of 1 : 2 : 4-trichlorobenzene, 52 grams of 1 : 2-dichlorobenzene, and 86 grams of chlorinated derivatives boiling between 200 and 230°.

The chlorination is probably expressed by the following equation:—

$$C_6H_6 + SnCl_4 = C_6H_5Cl + HCl + SnCl_2,$$

the stannic chloride being regenerated continuously during the reaction by the current of chlorine. The author claims that this method is superior to the ordinary iodine process, since only substitution-products are formed, and the necessity of separating iodo-derivatives is avoided, whilst the time occupied in carrying out the process is shorter. T. G. N.

Conversion of Paradichlorobenzene into Metadichlorobenzene. By ISTRATI (*Bull. Soc. Chim.* [3], **3**, 186—188).—When paradichlorobenzene (10 grams) is heated with lead peroxide (20 grams) in sealed tubes at 250—300°, oxygen is set free and oily drops of an aromatic liquid appear, which are extracted by a mixture of alcohol and ether, and separated from the unaltered paradichlorobenzene by recrystallisation. This substance, which becomes solid on standing, and melts at + 17°, is metadichlorobenzene. The conversion is also effected by heating with mercuric oxide, red lead, chromium oxide, or litharge.

Fuming nitric acid forms with the meta-derivative a resinous substance which softens at 65°, and melts at 70—75°, appearing to be the compound $C_6H_3Cl_2{\cdot}NO_2$ [1 : 3 : 5], described by Körner.

T. G. N.

Action of Fuming Nitric Acid on Hexachlorobenzene. By ISTRATI (*Bull. Soc. Chim.* [3], **3**, 184—186).—Tetrachloroquinone is formed when hexachlorobenzene (25 grams) is treated in a reflux apparatus with a mixture of fuming nitric acid (200 c.c.) and sulphuric acid (50 c.c.). After six hours' reaction, the mixture is boiled for seven hours, and the substance is deposited as a yellow powder from the nitric acid, and may be purified by a further treatment with nitric acid, and subsequent crystallisation from alcohol or benzene. Thus prepared, it sublimes at 270° without previous fusion. T. G. N.

Ethylxylenes. By J. STAHL (*Ber.*, **23**, 988—994; compare Abstr., 1887, 35).—The ethylxylenes have been already prepared

by the action of ethyl iodide and sodium on the monobromo-derivatives of the three xylenes.

Ethylxylene, [Me : Me : Et = 1 : 3 : 4], boils at 185—186°, and is soluble in sulphuric acid in the cold. The *trinitro*-compound crystallises from alcohol in white needles melting at 127°. The corresponding *tribromo*-derivative crystallises from alcohol in large, white, prismatic needles melting at 94—95°. The hydrocarbon yields xylic acid on oxidation.

Ethylxylene, [Me : Me : Et = 1 : 4 : 2], boils at 185°; it easily forms a sulphonic acid of the formula [Me : Et : SO_3H : Me = 1 : 2 : 3 : 4], which yields the corresponding *ethylxylenol;* this melts at 37°, and boils at 245°; its alcoholic solution gives an intense green colour with ferric chloride. By prolonged fusion of the above sulphonic acid with potash, an acid is obtained in small quantity which melts at 140—142°, and has the constitution

[Me : COOH : OH : Me = 1 : 2 : 3 : 4]

(compare Abstr., 1884, 1347). Isoxylic acid, [Me : COOH : Me = 1 : 3 : 4], is formed by the oxidation of the hydrocarbon.

Ethylxylene, [Me : Me : Et = 1 : 2 : 4], boils at 187—188°. The trinitro-derivative crystallises from alcohol in slender needles melting at 121°. The *tribromo*-compound also crystallises in needles melting at 93°. Two ethylxylenes, [Me : Me : Et = 1 : 3 : 4] and [Me : Me : Et = 1 : 3 : 5], are formed by the action of ethyl bromide and aluminium chloride on metaxylene. The compounds were isolated by converting them into the sulphonamides, and separating the mixed crystals mechanically. J. B. T.

Action of Sulphuric Acid on Tribromophenol. By Georgesco (*Bull. Soc. Chim.* [3], **3**, 193—195).—Tribromophenol (60 grams) is heated with sulphuric acid (200 c.c.) for 20 hours, and, on cooling, the mixture is poured into water, and the dark-coloured precipitate collected. This contains a mixture of bromofrancëins which contain from 42—63 per cent. of bromine, and, in addition, tri-, tetra-, and penta-bromophenols. The results obtained by Istrati (this vol., p. 51) in respect to the migration of halogen-atoms in the benzene nucleus caused by sulphuric acid are thus confirmed, although the migration appears to be more easily effected with the bromine-derivatives than with the corresponding chlorine compounds. T. G. N.

Thymol-derivatives. By G. Mazzara and E. Vighi (*Gazzetta*, **19**, 335—336).—*Amidobromothymol ethyl ether*, $C_6HPrMeBr(NH_2)\cdot OEt$ [4 : 1 : 2 : 5 : 3], is prepared by reducing the ethyl ether of nitrobromothymol with tin and hydrochloric acid; on adding excess of sodium carbonate to decompose the hydrochloride formed, a liquid separates, which may be isolated by extraction with ether; it is a very heavy, red oil, which volatilises with difficulty in a current of steam. The *hydrochloride* crystallises from alcohol acidified with hydrochloric acid, in small, colourless, transparent prisms melting at 200—201°.

Orthobromothymol ethyl ether, $C_6H_2PrMeBr\cdot OEt$ [4 : 1 : 2 : 3], is

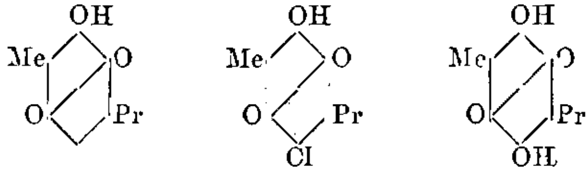
obtained by heating amidobromothymol ethyl ether (5 grams) with alcohol saturated with ethyl nitrite (50 grams) on the water-bath until the reaction subsides. The alcohol is then removed by evaporation, and the product distilled in a current of steam, when the ether passes over as a yellowish oil with an agreeable odour.

S. B. A. A.

Constitution of Derivatives of Carvacrol, Thymoquinone, and Thymol. By G. MAZZARA (*Gazzetta*, **19**, 337—343).—*Bromonitrosocarvacrol*, $C_6HPrMeBr(NO)\cdot OH$ [$OH : Pr : NO_2 : Me = 1 : 3 : 4 : 6$], is prepared by gradually mixing strongly cooled solutions of bromine (8·20 grams) and nitrosocarvacrol (10 grams) in glacial acetic acid; after a time, the product is poured into water, and the precipitate purified by dissolving it in ammonia, reprecipitating with sulphuric acid, and recrystallising twice from alcohol. It forms large, yellow, transparent, rhombic tables which melt at 166—168°, and are soluble in ether and in benzene.

Bromamidocarvacrol is prepared by reducing the preceding compound with tin and hydrochloric acid, decomposing the hydrochloride formed with a solution of sodium carbonate, and extracting the precipitate with light petroleum. The base is a yellowish-red oil, which changes, after a few days, into a solid mass; this softens at 53° and melts at 60—61°. When bromamidocarvacrol hydrochloride is oxidised with ferric chloride, and distilled in a current of steam, a yellow solid passes over, identical with the bromothymoquinone melting at 48°.

The author considers bromamidocarvacrol to have the constitution [$OH : Pr : NH_2 : Br : Me = 1 : 3 : 4 : 5 : 6$], and hydroxythymoquinone, the chloroxythymoquinone obtained by successively reducing and oxidising chlorodinitrocymene, and the dihydroxythymoquinone derived from the preceding compound to have respectively the formulæ I, II, and III:—



I. II. III

As the hydroxythymoquinone I may also be obtained from phenylazo- and phenyldisazo-thymol (Abstr., 1885, 1131), these compounds must respectively have the constitutions [$Me : OH : Pr : PhN_2 = 1 : 3 : 4 : 6$] and [$Me : PhN_2 : OH : Pr : PhN_2 = 1 : 2 : 3 : 4 : 6$].

S. B. A. A.

Trisubstituted Derivatives of Benzene. By V. WENDER (*Gazzetta*, **19**, 225—235).—Dry finely-powdered metanitracetanilide melting at 143° (10 grams) is gradually stirred into a mixture of fuming nitric acid (60 c.c. of sp. gr. 1·52) and concentrated sulphuric acid (60 c.c.), placed in a mixture of ice and salt, and allowed to remain until solution is complete. The solution is then removed from the freezing mixture, and, after the lapse of an hour, is poured

on to pounded ice; the viscous mass which separates is washed with water and repeatedly crystallised from boiling alcohol, when a dinitracetanilide is obtained in needles melting at 186°. On concentrating the alcoholic mother liquors to a small bulk, separating the precipitated dinitracetanilide, evaporating the greater part of the alcohol, and diluting with water, a yellow oil is deposited, which rapidly changes into a crystalline mass. When this is boiled for an hour with excess of acetic chloride, the product dissolved in alcohol and allowed to cool, the first deposit consists of the dinitracetanilide melting at 186°; subsequently, another acetanilide is deposited which, after purification, crystallises in needles melting at 121°. The last crop of crystals consists of a mixture of the preceding substance, with brown, nodular aggregates; the latter may be mechanically separated, and when crystallised from very dilute alcoholic solutions, form pale-yellow, polyhedral crystals melting at 144°. All these substances are dinitracetanilides. The yield from 100 grams of nitraniline consists of 50 grams of the product melting at 186°, 30 grams of the isomeride melting at 144°, and 6 grams of the third isomeride.

On heating a solution of these compounds in concentrated sulphuric acid for a few minutes at 110°, and diluting with water, the respective dinitranilines are precipitated. On warming with potash, ammonia is evolved, and the corresponding phenols are formed.

1.2.3-*Dinitraniline* is obtained from the acetanilide melting at 186°. It crystallises from water and alcohol in lustrous, orange-yellow needles which melt at 127°, and dissolves freely in warm alcohol and in acetic acid. It is moderately soluble in ether, sparingly so in boiling water, and only very sparingly in cold water. By treatment with acetic anhydride, it is acetylated with difficulty, but readily when boiled with acetic chloride. On heating with a solution of potash, ammonia is evolved, and the phenol-derivative is formed with partial resinification. It readily dissolves both in concentrated and in boiling dilute sulphuric acid. The *sulphate* is obtained in lustrous, colourless needles and slender prisms on adding an excess of sulphuric acid to the acetic acid solution of the dinitraniline. The *hydrochloride* is obtained as a white powder by passing a current of dry hydrogen chloride into an ethereal solution of the base; both these salts are decomposed by cold water. As this dinitraniline yields orthonitrobenzene when treated with ethyl nitrite, its constitution must be either $NH_2:(NO_2)_2 = 1:2:3$ or $1:3:4$; the latter supposition is inadmissible, as it would require the formation of a dinitrobromobenzene melting at 59·4° when bromine is substituted for amidogen.

1.2.3-*Dinitracetanilide*, $C_6H_3(NO_2)_2 \cdot NHAc$, crystallises from alcohol in flattened or prismatic, lustrous, colourless needles which melt at 186°, and are freely soluble in boiling alcohol, but only sparingly in cold alcohol, ether, chloroform, or benzene. When heated with potash, it loses ammonia. It is easily saponified by hot concentrated sulphuric acid.

1.2.3-*Dinitrobromobenzene* is obtained by mixing a solution of the dinitraniline melting at 127° (5 grams) in boiling sulphuric acid

(50 per cent.) with a boiling strongly acid solution of cuprous bromide, gradually adding a saturated aqueous solution of potassium nitrite (2·5 grams), heating for a few minutes, and diluting with water. The product is distilled in a current of steam, and crystallises from alcohol in lustrous, pale-yellow laminæ having an odour of bromonitrobenzene; it melts at 101·5°, and distils over unchanged at about 320°. It is freely soluble in boiling alcohol, only moderately so in cold alcohol and in ether; it dissolves very sparingly in boiling water. On heating dinitrobromobenzene with alcoholic ammonia in a sealed tube for four hours at 160°, a substance is obtained which crystallises from alcohol in yellow needles; this melts at 65—75°, and, probably, consists of a mixture of a bromonitraniline and a dinitraniline.

1 . 2 . 3-*Dinitroiodobenzene.*—Concentrated sulphuric acid (6 c.c.) is added to a solution of the dinitraniline melting at 127° (5 grams) in hot glacial acetic acid (70 c.c.); the whole is cooled down to 0° and constantly agitated to separate the sulphate of the base in a finely divided state; a cold saturated solution of potassium nitrite is now stirred in, and the solution of the diazo-salt is diluted with a little ice-cold water, and poured into a solution of potassium iodide acidified with hydriodic acid; the mixture is then heated in the water-bath for several hours, and, after standing for 12 hours, collected, washed, and freed from iodine with sodium hydrogen sulphite. By repeated crystallisations from alcohol it is obtained in flattened, lustrous, pale-yellow needles which melt at 138°, and can be distilled without decomposition. It is freely soluble in warm alcohol, but only very moderately in ether; it dissolves in concentrated sulphuric acid or nitric acid without undergoing any change, and it is only very slowly acted on by a boiling solution of potash.

1 . 3 . 6-*Dinitraniline*, prepared from the acetanilide melting at 121°, crystallises from boiling water and from alcohol in slender, lustrous, orange-yellow needles which melt at 137°, and are freely soluble in warm alcohol, but only sparingly in boiling water, and very slightly in cold water. In other respects, it closely resembles the 1 . 2 . 3-compound; its constitution is established by the formation of paradinitrobenzene when it is treated with ethyl nitrite.

1 . 3 . 6-*Dinitracetanilide*, obtained as previously described by the nitration of metanitracetanilide, crystallises from alcohol in beautiful white or slightly yellowish, silky needles, which melt at 121°, and dissolves freely in warm alcohol, and moderately in boiling water. It is easily attacked by aqueous potash, ammonia being evolved.

1 . 3 . 4-*Dinitraniline*, obtained from the acetanilide melting at 144°, crystallises from boiling water in slender, bright, lemon-yellow needles, and from alcohol in lustrous or brownish-yellow, prismatic needles. It melts at 154°, and dissolves very freely in alcohol and in acetic acid, but only sparingly in ether. It gives off ammonia when heated with potash, dissolves in concentrated sulphuric acid, and is precipitated unchanged on dilution. The *sulphate* is precipitated in beautiful, lustrous, colourless prisms by adding sulphuric acid to the acetic solution of the base, and allowing the whole to remain. It is decomposed by cold water. The base cannot be acetylated by the

action of boiling acetic chloride. Its constitution is demonstrated by the formation of orthodinitrobenzene when it is treated with ethyl nitrite.

1 . 3 . 4-*Dinitracetanilide* is obtained in hard nodules consisting of slender needles when its solution in boiling alcohol is rapidly cooled; when the solution is slowly cooled or allowed to evaporate, lustrous, yellowish, rhombic crystals are obtained, which melt at 141°, dissolve freely in warm alcohol, and moderately in boiling water.

1 . 3 . 4-*Dinitroiodobenzene* is prepared like the 1 . 2 . 3-compound. It crystallises from alcohol in thin, lustrous, canary-yellow needles which melt at 74·4°; it dissolves very freely in hot alcohol, ether, and chloroform, but only very sparingly in boiling water. When heated in a sealed tube with alcoholic ammonia for four hours at 170°, an iodonitraniline is obtained in pointed, brown needles, with violet lustre. This compound melts at 174°, dissolves freely in warm alcohol, and has very feeble basic properties. It appears to have the constitution $NH_2 : I : NO_2 = 1 : 3 : 6$, since it is converted into pariodonitrobenzene by boiling with ethyl nitrite and alcohol. S. B. A. A.

Action of Benzylamine on Methylene Chloride. By K. KEMPFF (*Annalen*, **256**, 219—232). — Methylenedibenzylamine. $CH_2(NH{\cdot}CH_2Ph)_2$ is formed when methylene chloride is heated with benzylamine at 100° for 12 hours. The product is treated with water to free it from benzylamine hydrochloride, the insoluble oil extracted with ether, and kept for some time over sulphuric acid, whereon the methylenedibenzylamine separates in crystals. It forms colourless, rhombic prisms, melts at 45—46°, and boils at 225—230° with partial decomposition; it is insoluble in water, but readily soluble in alcohol and ether; it reduces silver and mercury salts at the ordinary temperature. The *hydrochloride*, $C_{15}H_{18}N_2,2HCl$, crystallises from hot water in colourless, monoclinic plates, and melts at 240—242°. The *hydrobromide*, $C_{15}H_{18}N_2,2HBr$, crystallises from alcoholic ether in silky plates. The *hydriodide*, $C_{15}H_{18}N_2,2HI$, crystallises from benzene in colourless plates, and is more sparingly soluble in water and alcohol than the two preceding salts. The *sulphate*, $C_{15}H_{18}N_2,H_2SO_4 + 2H_2O$, crystallises in colourless prisms which effloresce on exposure to the air; the acid sulphate and the nitrate are deliquescent. The *phosphate*, $C_{15}H_{18}N_2,2H_3PO_4$, crystallises in needles, and melts at 228—233°. The *platinochloride*, $C_{15}H_{18}N_2,H_2PtCl_6$, crystallises in pale-yellow, monoclinic plates; the *aurochloride*, $C_{15}H_{18}N_2,2HAuCl_4$, in golden needles. The *oxalate*, $C_{15}H_{18}N_2,2C_2H_2O_4$, forms colourless crystals, and melts at 133—136°. The *picrate*, $C_{15}H_{18}N_2,2C_6H_3N_3O_7$, crystallises in light-yellow needles, and is very sparingly soluble in alcohol and water.

When methylenedibenzylamine hydrochloride is treated with potassium nitrite, the nitrite of the base seems to be formed.

F. S. K.

Action of Methylene Chloride on Para- and Ortho-toluidine. By H. GRÜNHAGEN (*Annalen*, **256**, 285—313).—A solid and a liquid methylenediparatoluidine are formed, together with a small quantity

of dimethylenediparatoluidine (see below), when paratoluidine is heated with methylene chloride at 100° for about 34 hours. The product is treated with water to dissolve the hydrochlorides of paratoluidine and dimethylenediparatoluidine, and the two compounds in the residual oil are partially separated by treatment with ether, in which the solid methylenediparatoluidine is only sparingly soluble; the liquid compound, on keeping, deposits more of the solid substance.

The liquid *methylenediparatoluidine*, $C_{15}H_{18}N_2$, boils at 350° with decomposition, and is readily soluble in most ordinary solvents except water; it dissolves in sulphuric acid with a green coloration. The basic *hydrochloride*, $C_{15}H_{18}N_2,HCl$, is a brown, amorphous, unstable compound, readily soluble in alcohol, but only sparingly in water; all the other salts are likewise amorphous. The *platinochloride*, $(C_{15}H_{18}N_2)_2,H_2PtCl_6$, and the *aurochloride*, $C_{15}H_{18}N_2,HAuCl_4$, were analysed.

The solid *methylenediparatoluidine*, $C_{15}H_{16}N_2$, is a colourless, amorphous compound, melts at about 156°, and boils above 350° with decomposition; it is only sparingly soluble in ether and alcohol, and insoluble in water. It dissolves in warm dilute acids, but separates unchanged on cooling, or on adding alkalis; its solution in sulphuric acid shows a green fluorescence. All the salts except the acid oxalate are amorphous and unstable. The *hydrochloride*, $C_{15}H_{18}N_2,2HCl$, is soluble in alcohol and water. The *platinochloride*, $C_{15}H_{18}N_2.H_2PtCl_6$, *aurochloride*, $C_{15}H_{18}N_2,2HAuCl_4$, and the *oxalate*, $C_{15}H_{18}N_2,2C_2H_2O_4$, were analysed.

Dimethylenediparatoluidine, $C_6H_4Me\cdot N<\begin{matrix}CH_2\\CH_2\end{matrix}>N\cdot C_6H_4Me$, separates from ether in crystals, melts at about 90 with previous softening, and is soluble in alcohol, but insoluble in water. The *hydrochloride*, $C_{16}H_{18}N_2 2HCl$, is a yellow, crystalline compound readily soluble in water and alcohol. The *aurochloride*, $C_{16}H_{18}N_2,2HAuCl_4$, is a yellow, crystalline compound readily soluble in water and alcohol. The *hydrobromide*, $C_{16}H_{18}N_2,2HBr$, is crystalline and readily soluble in water. The *sulphate*, $C_{16}H_{18}N_2,H_2SO_4$, crystallises in ill-defined plates, and is only sparingly soluble in water. The *isonitroso*-derivative, $C_{16}H_{17}N_3O$, is formed when dimethylenediparatoluidine is treated with nitrous acid. It is a yellow, crystalline powder, readily soluble in alcohol and ether, but insoluble in water, and it does not give Liebermann's nitroso-reaction. The *platinochloride*,

$$(C_{16}H_{17}N_3O)_2,HPtCl_6,$$

is a yellow, crystalline compound.

A liquid *methylenediorthotoluidine*, $C_{15}H_{18}N_2$, and the solid compound described below are formed when orthotoluidine is heated with methylene chloride at 110—115° for 10 hours. It is a thick, brown oil, boils at 350° with decomposition, and is readily soluble in alcohol and ether, but insoluble in water. The *platinochloride*

$$(C_{15}H_{18}N_2)_2,H_2PtCl_4,$$

and all the other salts are amorphous.

Solid *methylenediorthotoluidine*, $C_{15}H_{18}N_2$, separates from alcohol in rhombic crystals, $a : b : c = 0.7181 : 1 : 1.0623$, melts at about 135°, and is very sparingly soluble in water, and only sparingly in cold ether and alcohol. The salts are all readily soluble in water, moderately stable, and crystalline. The *hydrochloride*, $C_{15}H_{18}N_2,2HCl$, *hydrobromide*, $C_{15}H_{18}N_2,2HBr$, *phosphate*, $C_{15}H_{18}N_2,2H_3PO_4$, *sulphate*, $C_{15}H_{18}N_2,H_2SO_4$, and the two *oxalates*, $C_{15}H_{18}N_2,3C_2H_2O_4$ and $C_{15}H_{18}N_2,2C_2H_2O_4$, were analysed. F. S. K.

Action of Phenylhydrazine on Acetylurethane. By A. ANDREOCCI (*Gazzetta*, **19**, 448—452).—When an aqueous solution of acetylurethane (1 part), phenylhydrazine hydrochloride (1·5 parts), and sodium acetate (2·5 parts) is heated for two hours on the water-bath and allowed to remain, an oily substance is first precipitated, but subsequently a crystalline deposit is formed; the residual solution on concentration yields a further quantity of oil. The solid compound is purified by recrystallisation from water, and by precipitating its solution in ethyl acetate with light petroleum; it crystallises from ethyl acetate in colourless, hexagonal tables, melts at 166—167°, dissolves very freely in ethyl acetate and in alcohol, moderately in ether and in hot water, but only sparingly in cold water. It gives a reddish-brown coloration with ferric chloride. It has the composition $C_9H_9ON_3$, the condensation presumably taking place according to the equation $C_6H_8N_2 + C_5H_9O_3N = C_9H_9ON_3 + H_2O + C_6H_5{\cdot}OH$; analogous to the formation of 1-phenyl-3-methyl-5-pyrazolone from ethyl acetoacetate and phenylhydrazine (Abstr., 1887, 601). The oil above mentioned changes on standing, or on treatment with boiling water, into the crystalline compound; it is probably the real hydrazone, and is analogous to the compound $CMe{<}^{CH_2{\cdot}COOEt}_{N_2HPh}$, obtained by Knorr (*loc. cit.*) from ethyl acetoacetate.

The crystalline compound somewhat resembles pyrroline in its chemical behaviour; it dissolves in the cold in solutions of potash, and is reprecipitated unchanged on addition of hydrochloric acid, or even by a current of carbonic anhydride; it crystallises unchanged from a solution in concentrated hydrochloric acid. It further resembles phenylmethylpyrazolone in forming both a neutral and an acid silver salt, the former, $C_9H_8ON_3Ag$, is insoluble in water; it is very stable and is not affected by moderate heating or by light; it melts at 200° with incipient decomposition; the acid salt, $C_9H_8ON_3Ag + C_9H_9ON_3$, melts without decomposition. The author considers the new compound to be a derivative of an hypothetical pyrroline, $\begin{matrix} N{:}CH \\ | \\ N{:}CH \end{matrix}{>}NH$, which he terms pyrrodiazole, and accordingly to have the constitution $\begin{matrix} NPh{\cdot}CO \\ | \\ N : CMe \end{matrix}{>}NH$, 2-methyl-4-phenylpyrrodiazolone.

On heating the sodium-derivative of this substance with methyl iodide, a methylated compound is obtained which bears the same relation to it as antipyrine bears to Knorr's phenylmethylpyrazolone. It crystallises from water in long, acicular prisms which melt at 83°;

like antipyrine, it is readily soluble in water, alcohol, and chloroform. but only very sparingly in ether and in light petroleum.

S. B. A. A.

Phenyl-γ-hydroxybutyramide. By R. FITTIG and L. J. MORRIS (*Annalen*, **256**, 155—157; compare Fittig, Abstr., 1884, 744, and this vol., p. 879).—Phenyl-γ-hydroxybutyramide, $C_{10}H_{13}O_2N$, crystallises from alcohol in large, transparent, anhydrous, monoclinic prisms melting at 86°, and from water in colourless prisms containing 1 mol. H_2O, which it loses at 50°; it is very easily soluble in alcohol and hot water, and readily in chloroform, but more sparingly in ether. The hydrochloride, $C_{10}H_{13}O_2N.HCl$, crystallises in colourless, hygroscopic needles, and is very unstable.

F. S. K.

Substituted Phthalimides and their Conversion into the corresponding Primary Amines. By A. NEUMANN (*Ber.*, **23**, 994—1002).—*Desylphthalimide*, $COPh{\cdot}CHPh{\cdot}N{:}C_8H_4O_2$, is obtained by the action of potassium phthalimide on desyl bromide, $COPh{\cdot}CHPhBr$; it is deposited from hot glacial acetic acid in small, slightly yellow crystals which melt at 157—158°. *Desylphthalamic acid*, $COPh{\cdot}CHPh{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, is prepared from desylphthalimide by hydrolysis; it is best purified by dissolving in dilute ammonia, and reprecipitating with hydrochloric acid. By heating with concentrated hydrochloric acid, desylphthalamic acid is decomposed into *desylamine*, $COPh{\cdot}CHPh{\cdot}NH_2$, and phthalic acid. *Desylamine hydrochloride* is precipitated from solution by the addition of concentrated hydrochloric acid; it forms small, white needles melting at 210°. Both the salt and the free base are extremely unstable. The *platinochloride*, $(C_{14}H_{13}NO)_2,H_2PtCl_6$, is obtained in yellowish-brown crystals melting at 192—193°. The picrate is very insoluble. In all probability desylamine is identical with the compound obtained by E. Braun (Abstr., 1889, 613) by the reduction of benzilmonoxime.

Isoamylphthalimide is prepared by heating together isoamyl bromide and potassium phthalimide; it is a colourless liquid boiling at 307—308°. *Isoamylphthalmic acid*, melting at 114—115°, is obtained by hydrolysis. It is decomposed by concentrated hydrochloric acid with formation of isoamylamine.

Isobutylphthalimide, $CHMe_2{\cdot}CH_2{\cdot}N{:}C_8H_4O_2$, is obtained in a similar manner from isobutyl bromide; it melts at 93°, and boils at 293—295°.

Allylphthalimide, from allyl bromide, melts at 70°, and boils at 295°; it combines directly with 2 atoms of chlorine or bromine; the dichloro-compound crystallises from hot alcohol in needles melting at 93°. By the action of nitrous acid on allylphthalimide, an exceedingly unstable compound of an intense blue colour is formed; the colour disappears on drying, and by treatment with dilute acetic acid a substance with the formula $C_{11}H_{10}N_2O_5$ crystallises out in small, white leaves melting at 172—173°. This compound is stable, and is probably *hydroxynitropropylphthalimide*, $C_8H_4O_2{:}N{\cdot}CH_2{\cdot}C_2H_3(NO_2){\cdot}OH$, formed by the action of water on dinitropropylphthalimide, with the elimination of nitrous acid.

Methylenediphthalimide, $CH_2{:}(N{:}C_8H_4O_2)_2$, is obtained from methyl-

ene iodide and potassium phthalimide; it is deposited from boiling glacial acetic acid in light-brown crystals melting at 226°, and yields phthalic acid and ammonium chloride by the action of concentrated hydrochloric acid. J. B. T.

Azocumic Chloride. By P. Alexéeff (*Bull. Soc. Chim.* [3], **3**, 206—207).—Azocumic acid (1 part) is heated at 50° with phosphorus pentachloride (2 parts), and the resulting crystalline mass is dissolved in ether and recrystallised. *Azocumic chloride*, $N_2(C_6H_3Pr{\cdot}COCl)_2$, thus prepared forms orange-red crystals of the monoclinic system, $a : b : c = 1{\cdot}5268 : 1 : ?$, $\beta = 53° 39'$, and melts at 135°. The substance is but slowly decomposed by water or alkalis, and yields with alcohols the salts previously described (Abstr., 1885, 390), and with ammonia an amide. The author's pupils have also prepared and are studying parazobenzoic chloride melting at 145·5°, and metazobenzoic chloride melting at 87—89°. T. G. N.

Action of Halogen Acids on Phenylbutyrolactone. By R. Fittig and L. J. Morris (*Annalen*, **256**, 157—159; compare Fittig, Abstr., 1884, 744).—*Phenylchlorobutyric acid*, $C_{10}H_{11}ClO_2$, prepared by treating phenylbutyrolactone with concentrated hydrochloric acid in the cold, separates from carbon bisulphide in large, monoclinic crystals and melts at 70°. *Phenylbromobutyric acid*, $C_{10}H_{11}BrO_2$, melting at 69°, and *phenyliodobutyric acid*, $C_{10}H_{11}IO_2$, can be obtained in like manner; the iodo-compound crystallises in colourless plates, melts at 77° with decomposition, and is very unstable. F. S. K.

Preparation of Cinnamic Acid and its Homologues. By L. Claisen (*Ber.*, **23**, 976—978).—Ethyl cinnamate is obtained by slowly adding benzaldehyde (1 mol.) to sodium wire (1 at.), contained in excess of ethyl acetate. The mixture is allowed to remain a short time, and is then treated with water and acetic acid. After separating the aqueous solution and distilling off the unaltered ethyl acetate, an oily liquid is left which boils at 260—270°, and from which cinnamic acid is obtained by hydrolysis. The yield of ethyl cinnamate is 100—110 per cent. of the weight of the benzaldehyde employed. The same condensation is brought about by the action of sodium ethoxide in alcoholic or anhydrous ethereal solutions; the cinnamic acid obtained is however impure, and the yield is small. Ethyl benzalbutyrate is obtained in a similar manner from benzaldehyde and ethyl butyrate. This reaction may be explained by supposing that benzaldeyde, ethyl acetate, and sodium unite to form the sodium compound of ethyl phenylhydroxypropionate,

$$ONa{\cdot}CHPh{\cdot}CH_2{\cdot}COOEt,$$

and that the free ethereal salt obtained after acidifying is decomposed on distillation into ethyl cinnamate and water. J. B. T.

Preparation of Unsaturated Aromatic Acids. By L. Edeleano and Budisuteano (*Bull. Soc. Chim.* [3], **3**, 191—193).—Benzaldehyde (1 mol.), acetic chloride (1 mol.), and sodium acetate (3 mols.) are heated in a reflux apparatus at 160° for 24 hours. The mass obtained

is extracted with alkali, and an almost theoretical yield of cinnamic acid is obtained on acidifying with hydrochloric acid.

This combination of the methods of Bertagnini and Perkin is thus expressed :—

$$CH_3{\cdot}COCl + C_6H_5{\cdot}COH + nCH_3{\cdot}COONa = C_6H_5{\cdot}CH{:}CH{\cdot}COOH + CH_3{\cdot}COOH + NaCl + (n-1)CH_3{\cdot}COONa.$$

T. G. N.

Synthesis of Thymolcinnamic Acid. By L. NICOTERA (*Gazzetta*, **19**, 357—361).—Dry sodium thymolglycollate (92 grams), benzaldehyde (43 grams), and acetic anhydride (180 grams) are heated in a reflux apparatus for six hours at 150—160°, the product which, on cooling, solidifies to a mass of brown nodules consisting of minute needles, is boiled with water, allowed to cool, and the yellowish oil which separates heated with a 20 per cent. solution of sodium carbonate, extracted when cold with ether, and the alkaline residue acidified with hydrochloric acid. A white, flocculent substance is thrown down mixed with a yellow oil; the former is treated with light petroleum, the solution distilled, and the residue boiled for a few hours with baryta-water and alcohol; the barium salt thus obtained is purified and decomposed with hydrochloric acid, and the precipitate crystallised twice from alcohol. *Thymolcinnamic acid* obtained in this manner, forms minute, colourless, odourless needles melting constantly at 136°. On heating on platinum foil, it melts and volatilises without burning. It is very freely soluble in alcohol and in ether, only moderately in hot, and very sparingly in cold water. It probably has the constitution $CHPh{:}C(COOH)O{\cdot}C_6H_3MePr$. The *silver salt*, $C_{19}H_{19}O_3Ag$, is white, and changes a little on exposure to light, especially when damp. The barium salt, $(C_{19}H_{19}O_3)_2Ba + 2\frac{1}{2}H_2O$, crystallises in small, yellowish needles. S. B. A. A.

Phenylsalicylic Acid. By C. ARBENZ (*Annalen*, **257**, 76—87).—When phenylsalicylic acid, prepared by Graebe's method (Abstr., 1888, 477), is treated with phosphoric chloride (1 mol.) at 100°, it is completely converted into diphenylene ketone oxide (xanthone); concentrated hydriodic or hydrochloric acid at 180° brings about the same change.

Ammonium phenylsalicylate crystallises in long prisms, melts at 130°, and is readily soluble in water; it is decomposed by boiling water, and when heated alone, it is converted into diphenyl ether (m. p. 28°). The *potassium* salt crystallises in large rhombohedra, and is readily soluble in water. The *calcium* salt $(C_{13}H_9O_3)_2Ca + 2H_2O$, crystallises from hot water in needles, and loses its water at 180°. The *ethyl* salt, $C_{13}H_9O_3Et$, boils above 360°. The *phenyl* salt, $C_{13}H_9O_3Ph$, crystallises in slender needles, melts at 109°, and boils without decomposition; it is insoluble in water, but readily soluble in most organic solvents. The *amide*, $OPh{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$, prepared by treating the methyl or ethyl salt with aqueous alcoholic ammonia at the ordinary temperature, crystallises from alcohol in prisms, melts at 131°, distils without decomposition, and is readily soluble in

most organic solvents, but only sparingly in hot water; when treated with phosphoric anhydride, or hydrogen chloride, at 200—220°, it is converted into diphenylene ketone oxide. The *anilide*,

$$OPh\cdot C_6H_4\cdot CO\cdot NHPh,$$

is formed when the acid is heated with aniline at 110°, a little phosphorus trichloride added, and the mixture heated to 130°; it crystallises from alcohol in long needles, melts at 97°, and is very readily soluble in ether, benzene, and carbon bisulphide, but only sparingly in water and is insoluble in light petroleum; it distils without decomposition, and it is only slowly decomposed by alkalis. The *orthonitranilide*, prepared in like manner, crystallises in slender, yellow needles, melts at 121°, and is soluble in most ordinary solvents except water and light petroleum; on reduction with tin and hydrochloric acid, it is converted into the *anhydro-base*, $C_{19}H_{14}N_2O$, which crystallises from a mixture of ether and light petroleum in colourless needles, melts at 147°, and forms a sparingly soluble hydrochloride.

Dinitrodiphenylsalicylic acid, $C_{13}H_8O_3(NO_2)_2$, is obtained by nitrating phenylsalicylic acid in the cold, and purifying the product by means of the barium salt. It crystallises from benzene in colourless needles, melts at 153°, and is readily soluble in alcohol, acetic acid, and chloroform, but only sparingly in ether and benzene. The *barium* salt $(C_{13}H_7N_2O_7)_2Ba + 4H_2O$, crystallises in yellow plates, loses its water at 120°, and is only sparingly soluble (0·267 in 100 parts at 17°) in cold, but more readily in hot water and alcohol. The *calcium* salt, with $4H_2O$, crystallises in plates, and is more readily soluble in water than the barium salt. The *silver* salt, $C_{13}H_7N_2O_7Ag$, crystallises from hot water, in which it is readily soluble, in needles, and is very explosive. The *methyl* salt, $C_{13}H_7N_2O_7Me$, crystallises in prisms, melts at 126°, and is readily soluble in alcohol and ether, but insoluble in carbon bisulphide and light petroleum. The *ethyl* salt, $C_{13}H_7N_2O_7Et$, crystallises in prisms, and melts at 76°. The *amide*, $C_{12}H_7N_2O_5\cdot CO\cdot NH_2$, crystallises in prisms, and melts at 166°. When dinitrosalicylic acid is warmed with excess of fuming nitric acid, it is decomposed into dinitrophenol [$OH : (NO_2)_2 = 1 : 2 : 4$] and nitrosalicylic acid [$COOH : OH : NO_2 = 1 : 2 : 5$]; when heated at 150° with concentrated sulphuric acid, it is converted into β-dinitroxanthone (dinitrodiphenylene ketone oxide) and a sulphonic acid.

Tribromophenylsalicylic acid, $C_{13}H_7Br_3O_3$, prepared by heating phenylsalicylic acid with excess of bromine at 150°, crystallises from glacial acetic acid in colourless needles, melts at 176°, and is readily soluble in alcohol and ether, but only sparingly in hot, and insoluble in cold water. The *silver* salt, $C_{13}H_6Br_3O_3Ag$, is amorphous and insoluble in water. The *ethyl* salt, $C_{13}H_6Br_3O_3Et$, crystallises from alcohol in prisms, and melts at 67°.

Tribromoxanthone (*tribromodiphenylene ketone oxide*), $C_{13}H_5Br_3O_2$, is obtained when the preceding compound is heated with concentrated sulphuric acid at 150°; it crystallises from benzene, sublimes in needles, and is readily soluble in chloroform and carbon bisulphide, but only sparingly in alcohol and ether, and insoluble in alkalis.

F. S. K.

Ethyl Phenylparaconate. By R. FITTIG and H. LEONI (*Annalen*, **256**, 63—87; compare preceding abstract).—*Ethyl phenylparaconate* is formed when phenylparaconic acid, prepared by the method previously described (Fittig and Jayne, *Annalen*, **216**, 100), is dissolved in alcohol and the solution saturated with hydrogen chloride; it is a heavy, colourless oil with an aromatic odour, and boils at 250—252° (25 mm.).

Phenylitaconic acid, CHPh:C(COOH)·CH_2·COOH, is obtained by treating ethyl phenylparaconate with sodium in dry ethereal solution, or, better, by boiling the ethereal salt (2 mols.) with an alcoholic solution of sodium (1 mol.) for three to four hours. In the latter case, as soon as the formation of a precipitate is at an end, the alcohol is evaporated, the residue treated with water, the unchanged ethyl phenylparaconate extracted with ether, and the aqueous solution boiled with soda for about half an hour, in order to hydrolyse the ethyl sodium phenylitaconate. The solution is then rendered strongly acid, and the precipitated acid separated by filtration. The acid filtrate, on evaporation, yields further quantities of phenylitaconic acid, a very small quantity of phenylparaconic acid and some succinic acid, formed by the decomposition of the phenylparaconic acid; the yield of phenylitaconic acid is about 85 per cent. of the theoretical. It separates from hot water in prismatic crystals and from very concentrated solutions in cauliflower-like aggregates, melts at 172°, and is readily soluble in hot water, but only sparingly in cold water, ether, and benzene, and very sparingly in carbon bisulphide and chloroform. The *barium* salt, $C_{11}H_8O_4Ba + 2\frac{1}{2}H_2O$, crystallises from boiling water, in which it is only very sparingly soluble with $\frac{1}{2}$ mol. H_2O, and from cold aqueous solutions with $2\frac{1}{2}$ mols. H_2O, which it loses at 110—120°. The *calcium* salt, $C_{11}H_8O_4Ca$, is a granular, crystalline compound even more sparingly soluble than the barium salt. The *silver* salt, $C_{11}H_8O_4Ag_2$, is only very sparingly soluble in hot, and almost insoluble in cold water. The *ethyl* salt, $C_{11}H_8O_4Et_2$, is a thick, colourless oil, and boils at 315°. When the acid is heated to about 181°, it is partially converted into the anhydride, which distils as a colourless oil, but on heating more strongly carbonic anhydride is evolved, and a hydrocarbon and a phenol-like substance pass over, together with unchanged phenylitaconic acid and a small quantity of a crystalline acid which is insoluble in water. When phenylitaconic acid is treated with concentrated hydrobromic acid in the cold, or boiled with concentrated hydriodic acid, only a trace of phenylparaconic acid is formed, almost the whole of the acid remaining unchanged; when boiled for half an hour with dilute (1 : 1) sulphuric acid, it yields the polymeric phenylisocrotonic acid (m. p. 179°) described by Erdmann (*Annalen*, **208**, 54), and a small quantity of phenylbutyrolactone, but about half the acid remains unchanged.

Phenylbromoparaconic acid, $C_{11}H_9BrO_4$ (14·43 grams) is obtained, together with the isomeric iso-acid (1·56 grams), when finely divided phenylitaconic acid (15·05 grams) is suspended in water and treated with bromine; the crystalline products are separated by filtration, washed with water, dried, and recrystallised from boiling chloroform, in which the iso-acid is the more readily soluble. It crystallises from

chloroform in long, rhombic prisms $a : b : c = 0.6538 : 1 : 1.6223$, melts at 99°, and is readily soluble in hot ether, hot benzene, and acetic acid, but only sparingly in light petroleum and insoluble in carbon bisulphide; it is decomposed by boiling water, and by sodium carbonate, with liberation of hydrogen bromide and carbonic anhydride, yielding benzoylpropionic acid, and when reduced with sodium amalgam in acetic acid solution, it is converted into phenylparaconic acid.

Phenylisobromoparaconic acid, $C_{11}H_9BrO_4$, crystallises from chloroform in large, colourless, rhombic plates $a : b : c = 0.5998 : 1 : 0.9756$, turns brown at 135°, and melts at 144° with decomposition; it is readily soluble in ether, glacial acetic acid, and hot benzene, but only very sparingly in carbon bisulphide. When treated with sodium amalgam in acetic acid solution, it is converted into phenylparaconic acid, and when boiled with water, it is converted into benzoylpropionic acid.

Benzoylpropionic acid (m. p. 116°) does not crystallise with 1 mol. H_2O, as stated by Burcker (*Ann. Chim. Phys.* [5], **26**, 433), and the barium salt is also anhydrous, whilst the calcium salt crystallises with 4 and not with 3 mols. H_2O, as stated by Burcker. The *silver* salt, $C_{10}H_9O_3Ag$, crystallises from boiling water, and is stable in the light. When benzoylpropionic acid is treated with sodium amalgam in alkaline solution, and the whole then boiled with hydrochloric acid, it is converted into phenylbutyrolactone, but small quantities of a colourless, amorphous, neutral compound, and an acid (m. p. 165°) are also produced; the acid melting at 165° crystallises from hot alcohol in colourless needles, is only sparingly soluble in ether, and is probably identical with the compound obtained by Pechmann by boiling benzoylpropionic acid with zinc-dust and acetic acid.

Bromophenylparaconic acid, $CO<\begin{matrix}CH_2\cdot CH\cdot COOH\\ O\ -\ CH\cdot C_6H_4Br\end{matrix}$, is obtained when phenylparaconic acid is suspended in water and treated with bromine (1 mol.). It crystallises from benzene in nacreous plates, melts at 141.5°, and is readily soluble in alcohol and light petroleum, and moderately easily in hot water, but only sparingly in carbon bisulphide; it is not decomposed by boiling water, and when treated with sodium amalgam, is reconverted into phenylparaconic acid.

F. S. K.

Phenylitaconic Acid. By R. Fittig and P. Röders (*Annalen*, **256**, 87—96).—Benzylsuccinic acid, $C_{11}H_{12}O_4$, is obtained when phenylitaconic acid is reduced with sodium amalgam, the solution being kept only slightly alkaline by the frequent addition of dilute sulphuric acid. It crystallises from hot water in plates, melts at 161°, and is readily soluble in hot water and alcohol, but only sparingly in benzene, chloroform, and cold water. This acid has been previously prepared by Perkin (Trans., 1888, 11) from benzylacetylenetetracarboxylic acid. The *silver* salt, $C_{11}H_{10}O_4Ag_2$, is very sparingly soluble in hot water, and darkens on exposure to the light or when boiled with water. The *calcium* salt, $C_{11}H_{10}O_4Ca$, is very sparingly soluble both in hot and cold water. The *barium* salt, with $\frac{1}{2}H_2O$, separates

as a powder when a cold concentrated aqueous solution is heated. The *anhydride*, $C_{11}H_8O_3$, prepared by distilling the acid, crystallises from light petroleum in needles, melts at 102°, and is readily soluble in chloroform, benzene, and ether, but only sparingly in light petroleum and carbon bisulphide.

Benzylethanetricarboxylic acid, $C_{12}H_{12}O_6$, can be prepared by treating ethyl sodiobenzylmalonate (b. p. 169°, 12 mm.) with ethyl chloracetoacetate in alcoholic solution and hydrolysing the product with alcoholic potash. It crystallises from warm water or dilute alcohol in small prisms, and is moderately easily soluble in ether, alcohol, and warm water, but insoluble in benzene, chloroform, and carbon bisulphide; when boiled with water or when heated to 130—160°, it is converted into benzylsuccinic acid (m. p. 161°). The *calcium* salt, $(C_{12}H_9O_6)_2Ca_3 + 6\frac{1}{2}H_2O$, separates from hot water in a flocculent condition, loses $4\frac{1}{2}$ mols. of water at 100°, and the remainder at 210°; it is more readily soluble in cold than in hot water. The *barium* salt, with $2\frac{1}{2}H_2O$, loses its water at 210°, and is insoluble in both hot and cold water. The *silver* salt, $C_{12}H_9O_6Ag_3$, is very sparingly soluble, and darkens on exposure to the light or when boiled with water.

F. S. K.

A New Reaction of Tannin. By C. Böttinger (*Annalen*, **256**, 341—344).—When tannin (1 part) is boiled with phenylhydrazine (1 part) in aqueous solution, a mixture of substances is obtained which is soluble in ether and hot water; on the addition of soda to the aqueous solution, phenylhydrazine is liberated, and a beautiful greenish-blue coloration is produced. The substance to which the coloration is due can be isolated as follows:—After boiling with phenylhydrazine for four hours, the solution is concentrated, the water decanted, the reddish residue dissolved in hot water, and the solution acidified with hydrochloric acid. A little ammonia is then added, the solution shaken well, decanted from impurities, concentrated by evaporation, extracted with ether, and evaporated to dryness; the residue is then extracted with boiling alcohol, and the solution mixed with ether, whereon phenylhydrazine hydrochloride is precipitated, and the new substance remains in solution. It crystallises from water in colourless stellate groups, turns yellow on exposure to the air, melts at 112°, decomposes at 130—140°, and is readily soluble in acetic acid, hot water, and alcohol, but only sparingly in ether and cold water; it is only slowly decomposed by concentrated hydrochloric acid. It is readily soluble in phenylhydrazine; if this solution is boiled with acetic acid, an oil is obtained which dissolves in soda with a beautiful greenish-blue coloration.

When tannin is boiled with phenylhydrazine and acetic or hydrochloric acid, and the solution then treated with soda, the same greenish-blue coloration is produced, but on shaking the solution in a test-tube, reddish-yellow stripes are also observed, probably owing to the formation of gallic phenylhydrazide.

Ammoniacal solutions of the tannin-derivative described above rapidly darken, becoming first light-blue, and then violet. In its aqueous solutions lime-water produces a blue, and baryta-water a greenish-blue precipitate; in boiling solutions, mercuric chloride gives

a colourless, silver nitrate a black precipitate. It gives the hydrazide reaction with concentrated sulphuric acid and ferric chloride, and with ferric chloride alone, first a blue, and then a green coloration is produced, whilst ammonium carbonate produces a violet coloration. This compound occurs in the decomposition-products of benzoyltannin and phenylhydrazine, and also in the extract of Italian sumach, but it could not be detected in the extract of oak-wood or oak-tan; the phenylhydrazine-derivatives obtained from the oak-extracts have a totally different constitution, and are decomposed by concentrated hydrochloric acid at 120°.

F. S. K.

Nitro-derivatives of the Indoles. By C. ZATTI (*Gazzetta*, **19**, 260—263).—*Dinitromethylketole*, $C_9H_7N_3O_4$, is prepared by gradually introducing methylketole (α-methylindole) into ten times its weight of concentrated nitric acid (sp. gr. 1·50) placed in a freezing mixture. When the reaction which ensues is completed, the product, which is a nearly solid, brownish-red mass, is freed from excess of nitric acid by filtration, and dried on a porous tile. It is then dissolved in alcohol, the solution decolorised with animal charcoal, concentrated, diluted with water, and allowed to remain for some time, when the dinitro-derivative crystallises out in orange-yellow needles, which blacken and decompose on warming, and deflagrate when suddenly heated on platinum foil. It is soluble in warm alcohol, ethyl acetate, and in acetic acid, less so in benzene and chloroform, and only very sparingly in boiling water. It has an acid reaction, and dissolves in the alkaline hydrates and carbonates. A silver salt can be obtained as a gelatinous, yellowish mass by dissolving the ketole in ammonia, diluting with water, and adding silver nitrate. An isomeride of dinitromethylketole is prepared by gently warming methylketole with nitric acid (sp. gr. 1·47) and diluting with water. The product, after washing and drying on a tile, is repeatedly crystallised from alcohol, decolorised with animal charcoal, and precipitated from a solution in acetic acid by largely diluting with water; it is thus obtained as a very light, white powder which decomposes on heating. It is more soluble in alcohol and ethyl acetate than its isomeride; it is sparingly soluble in benzene, and almost insoluble in water; it dissolves in acetic acid, and is reprecipitated unchanged on dilution. It dissolves in the alkaline carbonates, and forms sodium and silver salts like its isomeride.

S. B. A. A.

Diphenyl-derivatives. By J. KAISER (*Annalen*, **257**, 95—102). —*Diphenylphthaloylic acid*, $C_6H_4Ph{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, can be obtained by heating phthalic anhydride with diphenyl and aluminium chloride; it is best purified by means of the calcium salt. It crystallises in colourless needles, melts at 220°, and is readily soluble in hot alcohol, benzene, chloroform, and ether; it dissolves in cold concentrated sulphuric acid, yielding a deep red solution, from which it is precipitated unchanged on the addition of water, but when warmed with concentrated sulphuric acid, it seems to be converted into a sulphonic acid. The *calcium* salt, $(C_{20}H_{13}O_3)_2Ca$, separates from hot concentrated solutions in crystals; the *barium* salt is more sparingly soluble. The *silver* salt, $C_{20}H_{13}O_3Ag$, is moderately easily soluble in hot, but

only sparingly in cold water. The *methyl* salt separates from light petroleum as a colourless, crystalline powder, and melts at 85—90°.

The compound $\begin{matrix} C_6H_4 \text{——} C{\cdot}C_{12}H_9 \\ | \qquad\qquad \| \\ CO{\cdot}NPh{\cdot}N \end{matrix}$, prepared by heating the acid with phenylhydrazine at 160°, crystallises from alcohol in slender, colourless needles, melts at 192—194°, and is insoluble in alkalis; it dissolves in concentrated sulphuric acid with a yellow coloration. The compound $\begin{matrix} C_6H_4{\cdot}C{\cdot}C_{12}H_9 \\ | \qquad \| \\ CO{\cdot}O{\cdot}N \end{matrix}$, obtained by heating the acid with hydroxylamine hydrochloride in alcoholic solution, crystallises in plates, melts at 180°, and is readily soluble in chloroform, but only sparingly in alcohol; it dissolves in concentrated sulphuric acid with a yellow coloration, and it is soluble in warm alkalis.

Parahydroxydiphenyl (m. p. 160—162°) was prepared by diazotising paramidodiphenyl; it is identical with the compound obtained by Latschinoff (this Journal, 1873, 749), and also with the compound (m. p. 151—152°) obtained by Hübner (Abstr., 1882, 180). The *benzoyl*-derivative crystallises in colourless plates, melts at 150°, and is readily soluble in boiling toluene, but only sparingly in alcohol and ether. The *acetyl*-derivative, $C_{12}H_9{\cdot}OAc$, crystallises in plates, melts at 88—89°, and is readily soluble in alcohol and ether.

F. S. K.

Orthocresolbenzeïn. By O. DOEBNER and G. SCHROETER (*Annalen*, **257**, 68—75).—*Orthocresolbenzeïn*, $OH{\cdot}CPh(C_6H_3Me{\cdot}OH)_2$, is obtained by gradually adding benzotrichloride to orthocresol, and heating the mixture at 100° for several hours. The unchanged cresol is removed by distillation with steam, the residue dissolved in dilute soda, and the dye precipitated from the filtered solution with hydrochloric acid; the precipitate is then dissolved in a hot dilute solution of sodium sulphite, and the filtered solution boiled with dilute sulphuric acid to precipitate the dye. It is a dark-red powder, melts at 220—225°, and is readily soluble in glacial acetic acid and alcohol, but only sparingly in ether and cold benzene, and almost insoluble in water; it dissolves in alkalis yielding reddish-violet solutions, which become colourless on exposure to the air, or when warmed.

Dihydroxydimethyltriphenylmethane, $CHPh(C_6H_3Me{\cdot}OH)_2$, prepared by boiling cresolbenzeïn with sulphurous acid, crystallises from dilute alcohol in light-yellow needles, melts at 170—171°, and is readily soluble in alcohol, ether, benzene, and glacial acetic acid, but only sparingly in water; it is soluble in soda, and gradually turns red on exposure to the air. The *acetyl*-derivative, $C_{21}H_{18}(OAc)_2$, crystallises from dilute alcohol in yellowish needles, melts at 94°, and is readily soluble in alcohol, ether, benzene, and glacial acetic acid; it is quickly decomposed by warm alkalis, and by concentrated acids. The *benzoyl*-derivative, $C_{21}H_{18}(OBz)_2$, crystallises from dilute alcohol in colourless plates, melts at 91·5°, and is insoluble in water, but readily soluble in alcohol, ether, benzene, and glacial acetic acid. The *dibromide*, $C_{21}H_{18}O_2Br_2$, prepared by treating cresolbenzeïn with bromine in well-cooled glacial acetic acid solution, crystallises in compact, yellowish-red needles, melts at 130°, and is insoluble in water, and only sparingly

soluble in ether, but readily in alcohol, benzene, and glacial acetic acid. The *dinitro*-derivative, $C_{21}H_{18}O_2(NO_2)_2$, crystallises in bright-yellow plates, melts at 127°, and is readily soluble in benzene, alcohol, and glacial acetic acid, but only moderately easily in ether, and insoluble in water.

Dimethyldihydroxybenzophenone, $CO(C_6H_3Me·OH)_2$, is formed, together with benzene, when cresolbenzeïn is melted with potash. It crystallises from dilute alcohol in colourless needles, melts at 138°, and is readily soluble in alcohol, ether, and glacial acetic acid, but only sparingly in benzene; it is volatile at a temperature below its melting point.

Metacresol combines with benzotrichloride yielding a dye, but paracresol gives a colourless compound. F. S. K.

Pyrogallolbenzeïn. By O. DOEBNER and A. FOERSTER (*Annalen*, **257**, 60—68).—*Pyrogallolbenzeïn*, $C_{38}H_{24}O_{11}$, is obtained by heating pyrogallol with benzotrichloride, decomposing the chloride produced by boiling it with water, and repeatedly recrystallising the product from hot glacial acetic acid. It forms small, dark-green, hygroscopic crystals, which, when seen by transmitted light, are bright-red, and is almost insoluble in water, light petroleum, benzene, and carbon bisulphide, but more readily in alcohol, ether, hot chloroform, and hot sodium acetate, forming dark-red solutions. It dissolves in alkalis, ammonia, and alkaline carbonates; the neutral solutions are bluish-violet, but if a trace of free alkali is present the solutions are deep blue. It is partially decomposed by mineral acids; in neutral solutions of the ammonium salt most metallic salts produce bluish-violet, amorphous precipitates. The *acetyl*-derivative, $C_{38}H_{20}O_7(OAc)_4$, separates from hot alcohol in well-defined, bright-red crystals, melts at 208°, and is only sparingly soluble in cold alcohol and ether, and insoluble in water; it is quickly decomposed by warm soda. The *benzoyl*-derivative, $C_{36}H_{20}O_7(OBz)_4$, crystallises from hot alcohol or acetone in thin, red prisms, with a green reflex, melts at 251°, and is almost insoluble in water and ether. The compound $C_{38}H_{18}O_6(O·C_5H_9O_4)$, prepared by treating pyrogallolbenzeïn with valeric chloride at 160°, crystallises from alcohol and acetone in red needles with a green reflex, and melts at 227—228°. The *picrate* of pyrogallolbenzeïn crystallises in small, red needles.

Hydropyrogallolbenzeïn is obtained when pyrogallolbenzeïn is reduced with zinc-dust in glacial acetic acid solution. It crystallises from dilute acetic acid in reddish needles, turns red on exposure to the air, and loses 3 mols. H_2O at 110°; the anhydrous substance has the composition $C_{19}H_{14}O_5$, and is therefore an anhydride of hexahydroxytriphenylmethane. It dissolves in warm concentrated sulphuric acid with partial decomposition, yielding a violet solution of a sulphonic acid. F. S. K.

Chlorine Compounds of Tolane. By A. ELLOART (*Amer. Chem. J.*, **12**, 231—253).—According to Wislicenus' theory of geometrical isomerism, the central-symmetrical (β-) variety of tolane dichloride should be more stable than the plane-symmetrical (α-) variety.

To test this, the action of heat on these substances was studied. Tolane tetrachloride was prepared by treating benzile with excess of phosphorus pentachloride, and crystallising the product from light petroleum. It was converted by reduction with zinc into the dichlorides, and these were separated from each other in the manner detailed by Blank (Abstr., 1889, 261), and recrystallised from alcohol. The plane-symmetrical dichloride melted at 139·5°, the central-symmetrical at 58°. Two grams of each dichloride was placed in small tubes, and these in two larger tubes, which were sealed, and then heated side by side in an oven. The contents were dissolved in alcohol, and the solution was cooled and filtered; the crystals of the α-dichloride which collected on the filter were weighed, and so was the mixture of dichlorides obtained by evaporating the alcoholic filtrate. The weight of this latter was also ascertained, and the amount of the α-dichloride in the residue from this filtrate was then calculated, the solubility of the α- in alcoholic solutions of the β-variety having been determined by separate experiments. It was thus shown that the plane-symmetrical variety undergoes conversion much more easily than the other, as we should expect from the theory; the amount of conversion increased with the temperature and with the time, and reached a maximum at about 300°, at which temperature 68 per cent. of the α-variety was found to be converted into the β-, and only 32 per cent. of the β- into the α-variety. Moreover the relative amounts of α- and β-varieties converted at any temperature were approximately in the same ratio, namely, 68 : 32.

It is then shown that Blank's statement that a larger amount of plane-symmetrical dichloride is obtained then the theory requires (that is than one-third of the total dichlorides) is erroneous; if his results are corrected for the alteration in the solubility of the α-dichloride in alcohol caused by the presence of β-dichloride, the yield does not exceed the theoretical limit. Reasons are given for thinking that Blank's ditolane hexachloride, obtained by the action of zinc on tolane tetrachloride, was merely a mixture of tetrachloride and plane-symmetrical dichloride, which had crystallised out together.

It was further found that the plane-symmetrical dichloride is much more easily reduced with zinc-dust and alcohol than the central-symmetrical variety, and is hence the less stable variety, as Wislicenus' theory asserts. Also by chlorinating tolane, "ditolane hexachloride" was obtained; this has been shown to be a mixture of the tetrachloride and plane-symmetrical dichloride of tolane; hence the plane-symmetrical dichloride is the one obtained by the addition of chlorine to tolane, which is precisely what the theory requires. C. F. B.

Naphthylamidoacetic Acid. By O. FORTE (*Gazzetta*, **19**, 361—367).—Ethereal solutions of naphthylamine (2 mols.) and chloracetic acid (1 mol.) are mixed and agitated until the mass solidifies; excess of water is added and the ether distilled off; the product is then boiled for half an hour and concentrated, when a mixture of rose-coloured crystals with a brown resin is deposited. This is collected, repeatedly boiled with barium carbonate, and the filtered solution acidified, when naphthylamidoacetic acid,

$C_{10}H_7 \cdot HN \cdot CH_2 \cdot COOH$, is precipitated as a white powder. The yield is about 50 per cent. The acid crystallises from a mixture of alcohol and water in small, pale, rose-coloured needles which melt without decomposition at 192°, dissolve very readily in alcohol, moderately in acetic acid and acetone, sparingly in ether and benzene, and only very sparingly in hot water. It undergoes alteration on exposure to light and air, and is partially resinified by recrystallisation from alcohol. The aqueous solution gives a feebly acid reaction with litmus, reduces silver nitrate and mercury salts on heating, dissolves the oxides of silver and lead with difficulty, but has no action on the oxides of mercury or zinc. The *barium salt*, $(C_{12}H_{10}NO_2)_2Ba + 2H_2O$, crystallises in hemispherical tufts of small, rose-coloured prisms soluble in alcohol; the *copper salt*, $(C_{12}H_{10}NO_2)_2Cu$, is a brownish-red powder.

Acetylnaphthylamidoacetic acid, $C_{10}H_7 \cdot NAc \cdot CH_2 \cdot COOH$, is prepared by heating naphthylamidoacetic acid (15 grams), acetic anhydride (30 grams), and benzene (100 grams) for 14 hours. The product is freed from benzene, neutralised with sodium carbonate, and the solution decomposed with hydrochloric acid; a soft mass is precipitated, part of which is soluble in boiling water; the insoluble part contains a substance which melts at 220°. After some time, the aqueous solution deposits white prisms of acetylnaphthylamidoacetic acid, which melt at 154°, and leave no residue when ignited on platinum foil. This acid is freely soluble in alcohol, benzene, acetic acid, and acetone, but only sparingly in hot water and in ether. The aqueous solution has an acid reaction, and decomposes alkaline carbonates. The *barium salt*, $(C_{14}H_{12}NO_3)_2Ba + 5H_2O$, crystallises from aqueous solutions in stellate tufts of white, prismatic needles. It is more soluble in cold than in hot water.

S. B. A. A.

α- and β-Naphthylphenylene Ketone Oxide and Methyldiphenylene Ketone Oxide. By E. PHOMINA (*Annalen*, **257**, 87—95; compare this vol., p. 389).—*β-Phenylenenaphthylenemethane oxide*, $CH_2{<}{\substack{C_6H_4\\C_{10}H_6}}{>}O$, is obtained, together with naphthalene, when β-naphthaphenone oxide (Abstr., 1887, 152) is distilled over zinc-dust; it crystallises from alcohol, in which it is readily soluble, in plates, and melts at about 80°.

Hydroxy-α-naphthylhydroxyphenyl ketone (this vol., p. 389) melts at 103—106° (not 64—66°), and is very readily soluble in most organic solvents. The *methyl*-derivative, $C_{17}H_{10}OMe_2$, is a yellow, crystalline powder, melts at 64—66°, and is readily soluble in alcohol and benzene.

When methyl diphenylene ketone oxide (methyl xanthone) is melted with potash, it is converted into dihydroxymethylbenzophenone, but this compound could not be obtained in crystals.

F. S. K.

Compounds of Benzotrichloride with Phenols. By O. DOEBNER (*Annalen*, **257**, 56—60).—Benzeïns, analogous to phenolbenzeïn (Abstr., 1883, 861), are formed by the action of benzotrichloride on phenols, but only in the case of those in which the para-position to the hydroxyl-group is unoccupied.

α-Naphthabenzeïn, $C_{54}H_{38}O_5$, is prepared by heating benzotrichloride (1 mol.) with α-naphthol (1 mol.) at 100°. As soon as the evolution of hydrogen chloride is at an end, the chloride produced is boiled with dilute soda and the filtered solution acidified, whereon the α-naphthabenzeïn is precipitated in brownish-red flocks. It is purified by dissolving it in alcohol, precipitating with hydrochloric acid, and washing the precipitate with boiling water. It is a reddish-brown, amorphous powder, soluble in alcohol, ether, benzene, and glacial acetic acid, yielding yellowish-red solutions, but insoluble in hot water. It forms dark-green, amorphous compounds both with acids and alkalis, and when melted with potash it is decomposed into benzoic acid and α-naphthol. On reduction with zinc and acetic acid, it is converted into a colourless powder which seems to be dihydroxydinaphthylphenylmethane, $CHPh(C_{10}H_6{\cdot}OH)_2$. The constitution of naphthabenzeïn is probably expressed by the formula

$$CPh(C_{10}H_6{\cdot}OH)_2{\cdot}O{\cdot}CPh(C_{10}H_6{\cdot}OH)_2.$$

The compound $CPh(C_{10}H_7O)_2{\cdot}O{\cdot}CPh(C_{10}H_7O)_2$ is formed when β-naphthol is treated with benzotrichloride as described above. It crystallises from hot nitrobenzene in small, colourless needles, melts above 350°, distils with only slight decomposition, and is insoluble in water, alcohol, ether, benzene, &c.; it does not combine with acids or alkalis, and is decomposed by concentrated sulphuric acid into benzoic acid and β-naphthol. F. S. K.

Amidochrysene. By E. BAMBERGER and C. BURGDORF (*Ber.*, **23**, 1006—1007).—With reference to Abegg's statement that nitrochrysene cannot be reduced by the usual agents (this vol., p. 789), the authors state that nitrochrysene is reduced by tin and hydrochloric acid in the usual way.

Norwegian Oil of Caraway. By C. NICOLAYSEN (*Bied. Centr.*, 1890, 278—279).—Norwegian wild caraways contain more oil than the German seed (Christiania seed contains 6·1 per cent. of volatile oil, Tromsö 6·4 per cent). This oil is a mixture of carvol and carvene, the proportions varying with the locality of growth. Taking samples from three districts, the percentage of carvene averages 52, that of carvol 48, whilst the specific gravity averages 0·9053. The low specific gravity of Norwegian oil is due to the relatively high percentage of carvene. As regards rotatory power for sodium light at 16° in a tube of 10 cm., oil from Christiania gave + 8° 21′, Tromsö oil + 10° 12′, and Gudbrandsthal + 13° 6′.

Oil of juniper has also been examined; the percentage of ethereal oil in the ripe berries being 0·34 per cent. (Trondhjem), in unripe berries from Gudbrandsthal 1·73 per cent., and in sprays bearing ripe and unripe berries from Tromsö 1·91 per cent. E. W. P.

Santoninoxime and its Derivatives. By P. GUCCI (*Gazzetta*, **19**, 367—382).—Santoninoxime, $C_{15}H_{19}NO_3$, was first obtained by Cannizzaro (Abstr., 1886, 73). It is best prepared by boiling a mixture

of santonin (5 parts), hydroxylamine hydrochloride (4 parts), alcohol (50 parts), and precipitated calcium carbonate (3—4 parts) for 6—7 hours on the water-bath and adding an excess of boiling water to the clear solution. The yield is 80 per cent. of the santonin employed. It crystallises from alcohol in white, lustrous needles which melt at 216—219° with incipient decomposition, dissolves readily in alcohol and ether, but only very sparingly in boiling water, which, however, has no chemical action on it; it dissolves in hot solutions of the alkaline hydrates and carbonates, forming colourless solutions, from which it is precipitated unchanged on the addition of an acid. It is only very partially resinified by boiling with acetic acid, or dilute sulphuric acid, or concentrated hydrochloric acid, and the solution treated in this way has no reducing action on Fehling's solution. It is split up into its constituents on warming with very dilute hydrochloric acid, the santonin being quantitatively reproduced.

The *acetyl-derivative*, prepared by the action of acetic chloride or anhydride on the oxime, crystallises in minute needles which change in colour on heating to 70°, and decompose at 201—203°. It is soluble in warm glacial acetic acid, but is almost insoluble in the cold in that solvent and in alcohol, ether, benzene, &c. It dissolves in hot baryta-water, and on treating the solution with carbonic anhydride, filtering, and acidifying, the oxime is reprecipitated in a state of great purity. The pure oxime so prepared is lævogyrate, the specific rotatory power being $[\alpha]_D = -80.83$; for the crude oxime $[\alpha]_D = -82.47$.

The molecular weight of the oxime was confirmed by Raoult's method. The mother liquors from the oxime obtained in the ordinary way (from hydroxylamine and sodium acetate) also contain a substance which crystallises from absolute alcohol in thin, white aggregates which change colour at 210° and decompose at 228—231°. When sodium amalgam is gradually added to a solution of the oxime (20 grams) in 50 per cent. acetic acid ($2\frac{1}{2}$ litres), care being taken that the temperature does not rise above 50°, and the cold solution treated with ether, the extract only contains some acetic acid and resinous matters; the aqueous solution, however, after being heated to remove the ether, and concentrated in a vacuum, yields a deposit of iridescent plates and slender needles which may be separated by fractional crystallisation from 90 per cent. alcohol. The first deposit obtained is repeatedly crystallised from alcohol, and forms large, iridescent plates which melt at 152—153°; the subsequent deposit, similarly treated, yields opaque, white crystals which melt at 167·5—168·5°. These substances are isomerides, and have the molecular formula $C_{15}H_{18}O_2$; the isomeride crystallising in plates is produced alone if during the preparation heating is discontinued as soon as the crystallisation commences and the solution is then strongly agitated; protracted heating, on the other hand, leads to the formation of an excess of the second isomeride; this conversion may be directly effected by heating the plates with dilute acetic acid at 100°. Acetic anhydride has no action on either of the isomerides; hot solutions of the alkalis dissolve them both, and on prolonged heating the substance melting at 152—153° is converted into its isomeride. The

former is dextrogyrate, $[\alpha]_D = +30\cdot75$; the latter is lævorotatory, $[\alpha]_D = -73\cdot73$. S. B. A. A.

Santoninphenylhydrazone. By G. GRASSI-CRISTALDI (*Gazzetta*, **19**, 382—395).—*Santoninphenylhydrazone*, $C_{15}H_{18}O_2\!:\!C\!:\!N_2HPh$, is best prepared by boiling phenylhydrazine with an acetic solution of santonin for about 10 minutes; the deposit is purified by dissolving it in dilute hydrochloric or sulphuric acid and reprecipitating with an alkali. After repeated crystallisation from alcohol, it forms straw-coloured, shining needles which melt at 220—221° with decomposition. On gradually heating to 100°, it turns red, and is resinified; if plunged into sulphuric acid heated to 210°, its melting point rises to 224—225°. It is almost insoluble in the cold in the ordinary solvents, but dissolves on heating with alcohol, benzene, or glacial acetic acid, but only sparingly in ether. It is dextrogyrate, $[\alpha]_D = +152\cdot42$. It dissolves in boiling solutions of the alkaline hydrates or carbonates, and is reprecipitated unchanged on acidification; it also dissolves in cold concentrated sulphuric and hydrochloric acids; from the latter solution an orange-coloured *hydrochloride* is deposited on standing. This compound is unstable, turns yellow on exposure to the air, and is decomposed by contact with alcohol. The *platinochloride* $(C_{21}H_{24}O_2N_2)_2,H_2PtCl_6$, is a yellow, amorphous powder. These reactions show that santoninphenylhydrazone combines the basic properties of a hydrazone with the lactonic properties of santonin.

Hyposantonin, $C_{15}H_{18}O_2$, is prepared by reducing an alcoholic solution of the preceding compound with sodium amalgam. Santoninphenylhydrazone (10 grams) is dissolved in 80 per cent. alcohol (1500 c.c.), the solution is acidified with acetic acid, care being taken that the temperature does not exceed 50°; sodium amalgam is then gradually added. The solution becomes first red, then yellow; at this stage two-thirds of the alcohol is distilled off under reduced pressure and the reduction continued; more alcohol is then removed, &c. The product is poured into a large excess of water, the precipitate separated by filtration, the solution shaken with ether, and, after separation of the ethereal solution, concentrated on the water-bath; colourless, shining plates of hyposantonin then separate on the surface of the liquid. After recrystallisation from alcohol, this substance melts at 152° without decomposition, and sublimes unaltered in a current of carbonic anhydride. It is very freely soluble in benzene and in warm alcohol, ether, or acetic acid, but insoluble in water. Unlike santonin, it is not affected by exposure to light. It is dextrogyrate, the specific rotatory power $[\alpha]_D = +30\cdot06$. When the ethereal extract mentioned above is evaporated and the residue made alkaline and distilled in a current of steam, aniline passes over, and the residue consists of resinous matter and of a solution of the sodium salt of an acid, $C_{15}H_{24}O_3$; this acid crystallises from water in shining scales which melt at 152—153°, and can be volatilised unchanged in an atmosphere of carbonic anhydride. It is very freely soluble in ether, alcohol, benzene, acetic acid, or hot water, but only sparingly in cold water. It is dextrogyrate, the specific rotatory power $[\alpha]_D = +34\cdot64$. Hyposantonin is insoluble in

cold solutions of the alkaline hydrates and carbonates, but dissolves when heated with them; when a crystal is heated with a mixture of equal parts of sulphuric acid and very dilute ferric chloride, it dissolves, and after a time the liquid acquires a violet coloration, changing to green (distinction from santonin). When santoninphenylhydrazone is reduced with zinc and sulphuric acid, the product contains, besides hyposantonin, aniline, and resins, a compound which forms small, white crystals, melts at 235°, dissolves in hot ether and in alcohol, but is insoluble in acids and in alkaline carbonates.

Isohyposantonin is an isomeride of hyposántonin which is formed when that compound is heated with an excess of sulphuric acid, or precipitated from its alkaline solution by hydrochloric or sulphuric acid; it is best prepared by acidifying a hot solution of hyposantonin in baryta-water with hydrochloric acid. It crystallises from alcohol in shining, white pyramids belonging to the rhombic system, melts at 168·5°, and sublimes unchanged in a current of carbonic anhydride. It is less soluble in benzene and in alcohol than hyposantonin, but it is more soluble in hot water, and equally soluble in hot alkaline hydrates and carbonates. It is lævogyrate, the specific rotatory power $[\alpha]_D = -70° 31'$. S. B. A. A.

Alcoholic Extract of Yeast. By J. de Rey-Pailhade (*Bull. Soc. Chim.* [3], **3**, 171—174).—In previous communications (Abstr., 1888, 1101), the author has indicated the existence of a principle, philothion, occurring in alcoholic extract of yeast and in most animal and vegetable tissues. 1 litre of the extract prepared as previously described, when shaken with finely divided sulphur (1 gram), causes the formation of 10 milligrams of hydrogen sulphide. At 40°, the oxygen dissolved by the alcoholic extract (4·5 c.c. per litre) is absorbed in 4 to 5 hours, and the peculiar property of the liquid disappears. The extract when acidified with hydrochloric or sulphuric acid loses its properties, which are restored on neutralisation. Animal charcoal almost entirely removes the philothion. Carmine and indigo-carmine are decolorised by the alcoholic extract, the rapidity of the effect being increased by a previous addition of alkali. T. G. N.

Action of Chlorine on Hæmatoxylin and Logwood Extract. By W. W. Macfarlane and P. S. Clarkson (*Chem. News*, **61**, 160—162).—Logwood when "cured," that is, wetted and fermentation allowed to take place, is more active tinctorially, especially on wool, than the uncured wood. Various workers have investigated the cause of this, but without success. The authors now show that hæmateïn is produced, and doubtless accounts for the improvement. Experiments made by the authors indicate that when solutions of logwood extract are acted on by chlorine, the depth of colour obtained on wool mordanted with potassium dichromate and potassium hydrogen tartrate, increases with the quantity of chlorine used, up to a maximum, after which a dull and grey shade is produced. Less chlorine is required at 80° than at ordinary temperatures, and the

colour intensified by chlorine is quite as lasting as that from "cured" wood.

Experiments with hæmatoxylin gave similar results, and it was found that the best tinctorial development was obtained when the proportion of chlorine was 2 mols. to 1 mol. hæmatoxylin, or when the former amounts to 47 per cent. of the latter; with bleaching powder, however, half this quantity suffices. The product, by treatment with ether and chloroform, yielded a white, crystalline substance soluble in ether, chloroform, water, and acetic acid; a brownish, resinous substance readily soluble in ether, alcohol, and water, seemingly a chlorine substitution-product of hæmatoxylin or hæmateïn, which takes no part in the dyeing; and bright, bronzy-greenish scales with physical and chemical properties identical with those of hæmateïn. Salting out the product from the action of chlorine on hæmatoxylin yields resinous matters only.

Colouring matter from "cured" logwood, separated by means of alcohol and hydrochloric acid, is the same as hæmateïn obtained by the oxidation of hæmatoxylin in presence of ammonia. In comparative dyeing experiments on wool made with this colouring matter, hæmateïn prepared with chlorine, and hæmatoxylin, the shades from the two former were twice as full as that from the last mentioned, and the wood colouring proved slightly duller than the chlorine-hæmateïn. On cotton, with a bath containing 5 per cent. of colouring matter, 44 of sodium carbonate, 5 of sodium hydroxide, 1 of sodium sulphite, and 16 of copper sulphate, the reverse was the case: the hæmateïns being of little practical value with abundant precipitation in the bath, whilst hæmatoxylin gave darker shades with little or no precipitate. Hæmatoxylin reduces Fehling's solution more strongly, but more slowly than hæmateïn. D. A. L.

The Molecular Weight of Pyrrolene-derivatives. By G. Magnanini (*Gazzetta*, **19**, 251—260).—*αβ'-Dimethylpyrroline*, prepared from αβ'-dimethylpyrrolinedicarboxylic acid and purified by boiling with barium oxide for 12 hours, boils at 165·7 (corr.) at 765·0 mm. pressure. It gives normal results in dilute benzene solutions (up to about 3 per cent.), but rather high values with acetic acid or concentrated benzene solutions. The results are much closer when calculated by Arrhenius's method.

α-Acetylpyrroline melts, when pure, at 90·5° (corr.). Normal results were obtained from aqueous and from acetic acid solutions; benzene solutions, when not extremely dilute, gave very high values.

α-Pyrrolenecarboxylic acid is too sparingly soluble in benzene for the use of that solvent; the figures obtained from an acetic acid solution show a normal molecular weight, but are somewhat irregular on account of the marked exhibition of surfusion phenomena.

Methyl α-pyrrolinecarboxylate melts, when pure, at 73·2°, and gives normal results in dilute acetic acid solution. The values obtained from the acetic acid solutions of all the above compounds are normal when calculated according to Arrhenius.

Iodole (*tetriodopyrroline*) is only very sparingly soluble in acetic acid; the solution, however, gives normal results; extremely dilute

(under $\frac{1}{4}$ per cent.) solutions in ethylene dibromide likewise give normal values, but these rise very rapidly with increasing concentration of the solution. Curves are given showing the relation between the molecular weight and the depression of temperature for all the above compounds. From the foregoing results, it appears that all the pyrrolene-derivatives examined follow Raoult's law.

S. B. A. A.

Action of Ethyl and Propyl Iodides on Potassium Pyrroline. By C. W. Zanetti (*Gazzetta*, **19**, 290—297).—In a preceding communication (Abstr., 1889, 727, 1208), the author showed that the action of alcoholic iodides on potassium pyrroline resulted in the simultaneous formation of tertiary pyrrolines and of derivatives in which the alcohol radicle is united with carbon; the action of ethyl iodide thus gives rise to the compounds C_4H_4NEt, C_4H_3EtNH, and C_4H_3EtNEt. The following results were obtained from the further investigation of these compounds:—

1. *Ethylpyrroline*, C_4H_4NEt, obtained by the action of ethyl iodide on potassium pyrroline, and purified from traces of pyrroline and its higher homologues by boiling with freshly fused caustic potash, boils at 129—130° (corr.) at 762 mm.

Ethyldibromomaleïmide, $C_4Br_2O_2NEt$, is prepared according to the method indicated by De Varda (Abstr., 1889, 57), from the tetrabromo-1-ethylpyrroline described by Bell (Abstr., 1879, 525). The latter compound, which crystallises from alcohol in small, white needles melting at 83°, is very gradually added to three times its weight of nitric acid (sp. gr. = 1·49) cooled down to 0°; a brisk reaction takes place, and fumes of bromine are evolved, leaving a clear solution. On pouring the latter into excess of water, ethyldibromomaleïmide is deposited. By repeated crystallisation from dilute boiling alcohol, it may be obtained in small, yellowish needles which melt at 93—94°.

To determine whether the portion of the product of the action of ethyl iodide on potassium pyrroline, which combines with potash and boils at 150—190°, contains one or more ethylpyrrolines, it was heated in a reflux apparatus for 10 hours with sodium acetate and acetic anhydride. The product, after removal of the excess of acetic anhydride, yields a heavy oil, from which fractions were separated distilling over between 210—235° and 240—255° respectively.

The first fraction volatilises in a current of steam, and contains only 1-acetylpyrrolines, since no silver compounds are obtainable. A portion of this product distils over between 225° and 228°, and has the composition $C_4H_3EtN{\cdot}Ac$.

The fraction boiling between 240° and 255°, when strongly cooled in a mixture of ice and salt, yields a deposit which crystallises from alcohol in scales melting at 42—44°; it is probably identical with the ethylacetylpyrroline described by Dennstedt and Zimmermann (Abstr., 1886, 1043). The silver compound of this substance has the composition $C_4H_2EtAcNAg$. The liquid residue is freed from traces of 1-acetyl compounds and of pyrroline, and extracted with ether;

the extract contains an oil, soluble in water, which does not solidify when placed in a freezing mixture, and forms a silver compound also having the formula $C_4H_2EtAcNAg$.

The 1-*diethylpyrroline*, C_4H_3EtNEt, previously described by the author (*loc. cit.*), boils at 165—175° when pure.

The action of propyl iodide on potassium pyrroline resembles that of ethyl iodide, the only difference being that a smaller quantity of 1-propylpyrroline is formed. The portion of the product which combines with potash contains a mixture of propyl- and dipropylpyrrolines. Potassium pyrroline (20 grams) and propyl iodide (48 grams) are boiled together for three hours; after removing the excess of propyl iodide, an oil is obtained only a portion of which combines with caustic potash when boiled with it; the 1-propylpyrroline, which is not affected, is a colourless liquid boiling at 145·5—146·5° at 755·8 mm. pressure. On decomposing the potassium compound with water, distilling in a current of steam, and extracting the distillate with ether, an oil is obtained boiling at 140—220°; this can be separated by fractional distillation into a propylpyrroline, C_4H_3PrNH, passing over at 160—180°, and a mixture of a propylpyrroline with a dipropylpyrroline.

From the above experiments, it seems that the action of alcoholic iodides on potassium pyrroline is similar to that of the acid chlorides. The yield of tertiary pyrroline obtained with propyl iodide is smaller than that obtained with ethyl iodide, and this again smaller than that with methyl iodide; this probably depends on the temperature at which these iodides respectively boil, and renders it probable that no 1-pyrroline at all would be obtained if an iodide of a higher alcohol radicle were employed. S. B. A. A.

The Induline Group. By O. FISCHER and E. HEPP (*Annalen*, **256**, 233—263; compare Abstr., 1888, 1291 and 1890).—*Rosinduline* $\overset{4}{N}H{:}C_{10}H_5{<}{\overset{1}{N}\text{—}\atop \underset{2}{N}Ph}{>}C_6H_4$, is obtained when benzeneazo-α-naphthylamine hydrochloride (1 part) is heated with aniline (2 parts) and alcohol (4 parts) under pressure at 160—170° for six to eight hours. The alcohol is evaporated, the aniline distilled with steam, the solution filtered, and the residue, which also contains rosindone (see below) repeatedly extracted with boiling water; the combined filtrates are kept for a few days, decanted from resinous products, the solution acidified with hydrochloric acid, and carefully precipitated with sodium chloride. The *hydrochloride*, $C_{22}H_{15}N_3,HCl + 3\frac{1}{2}H_2O$, which separates from the solution in long, red needles, is decomposed with soda, and the base extracted with ether. It separates from cold ether in reddish-brown plates, melts at 198—199°, and is readily soluble in ether, benzene, and alcohol, but insoluble in water; its solutions absorb carbonic anhydride from the air.

Ethylrosinduline, $C_{24}H_{19}N_3$, prepared from benzeneazo-α-ethylnaphthylamine in like manner, crystallises in slender, green prisms, and melts at 184°.

Rosinduline and ethylrosinduline dissolve in concentrated sulph-

nric acid, yielding green solutions, the colour of which changes to red on the addition of water; alcoholic solutions of the bases show a yellowish-red fluorescence, and aqueous alcoholic solutions of the salts are fiery-red; both compounds are good dyes. When rosinduline is heated with concentrated hydrochloric acid at 160—180°, it is decomposed into ammonia and rosindone.

Rosindone, $C_{10}H_5O<\substack{N \\ NPh}>C_6H_4$, crystallises from a mixture of alcohol and toluene in red, hexagonal plates with a slight green fluorescence, and melts at 259°; it is insoluble in alkalis, but soluble in concentrated acids, and when distilled over zinc-dust in an atmosphere of hydrogen, is converted into α-naphthaphenazine (m. p. 142°), identical with the compound prepared by Witt.

Phenylrosinduline, $C_{28}H_{19}N_3$, has been previously described (Abstr., 1888, 1291) under the name of rosinduline. In addition to the methods already given, it can be prepared from the nitrosodimethyl-α-naphthylamine described by Friedländer and Welmans (Abstr., 1889, 150), and also, very conveniently, by mixing benzeneazo-α-naphthylamine hydrochloride (1 part) with hot aniline (2 parts), and immediately heating the mixture at 140—150° for four to five hours; if the mixture is first heated at 100—110° for some time, the principal product is tetranilidonaphthalene (see below). The product is treated with sodium carbonate, the aniline separated by distillation, and the residual phenylrosinduline extracted with boiling alcohol in order to free it from α-naphthaquinonedianil (see below). When heated with hydrochloric acid and a little glacial acetic acid at 200°, phenylrosinduline is converted into rosindone (m.p. 259°) and aniline; when rosindone is heated with aniline and a little aniline hydrochloride at 120—140°, it is reconverted into phenylrosinduline.

Paratolylrosinduline, $C_6H_4Me\cdot N{:}C_{10}H_5<\substack{N \\ NPh}>C_6H_4$, can be prepared from rosindone and paratoluidine in like manner; it crystallises from a mixture of chloroform and alcohol in brown needles, melts at 212—213°, and resembles phenylrosinduline in its properties. Its salts are of nearly the same shade as those of the phenyl-base. When heated at 200° with concentrated hydrochloric acid, it is decomposed into rosindone and paratoluidine.

Isoparatolylrosinduline, $NPh{:}C_{10}H_5<\substack{N \\ NPh}>C_6H_3Me$, is obtained when benzeazoparatolyl-α-naphthylamine hydrochloride (1 part) is heated with aniline (2 parts) and alcohol (4 parts) for several hours at 160—170°. It crystallises in reddish-brown plates, and melts at 231—232°; its salts resemble those of rosinduline.

Methylrosindone, $C_{23}H_{16}N_2O$, is formed, together with aniline, when isoparatolylrosinduline is heated with concentrated hydrochloric acid at 200°; it crystallises from boiling toluene in reddish-brown plates, melts at 255°, and is very similar to rosidone in its properties.

Trimethylphenylrosinduline, $C_6H_4Me\cdot N{:}C_{10}H_5<\substack{N\cdot C_6H_2Me_2 \\ N(C_7H_7)}$, is formed when nitrosoethyl-α-naphthylamine is treated with paratoluidine and its hydrochloride, as described in the preparation of phenyl-

rosinduline (*loc. cit.*) It crystallises from toluene in dark, bronze-coloured plates, and dissolves in concentrated sulphuric acid yielding a green solution which turns red on diluting; the red solutions of the salts have a shade more blue in them than those of phenylrosinduline.

Triparatoluidonaphthalene [$(NHC_7H_7)_3 = 1:2:4$] is obtained as a bye-product in the preparation of the preceding compound, and can be isolated by extracting the melt first with sodium carbonate and then with alcohol; it crystalises from alcohol or from a mixture of benzene and light petroleum in colourless needles, melts at 159—160°, and turns reddish on exposure to the air; it has only feeble basic properties. When boiled with mercuric oxide in benzene solution, or when treated with some other oxidising agent, it is converted into trimethylphenylrosinduline.

Toluidonaphthaquinoneditoluide, $C_{31}H_{27}N_3$, is formed as an intermediate product in the oxidation of triparatoluidonaphthalene to trimethylphenylrosinduline; it crystallises in orange-yellow plates and melts at 147°.

Naphthylrosinduline, $C_{10}H_7{\cdot}N{:}C_{10}H_5{<}{\genfrac{}{}{0pt}{}{N\overline{\quad}}{NPh}}{>}C_6H_4$, is formed, together with the isomeride described below, when benzeneazo-α-dinaphthylamine (1 part) is heated with aniline (2 parts) and alcohol (4 parts) at 160—170° for about 8 hours; both these compounds are also produced when nitroso-α-dinaphthylamine (1 part) is heated with aniline (2 parts) and aniline hydrochloride (1 part) at 110—120.° The deep-red product is treated with sodium carbonate, the alcohol and the aniline separated by distilling with steam, and the insoluble residue extracted with boiling alcohol, whereon napthylrosinduline remains undissolved, and the isomeride passes into solution. The two compounds can be readily distinguished, as the former dissolves in concentrated sulphuric acid yielding a blue, the latter yielding a green solution. Naphthylrosinduline crystallises from toluene in almost black needles, melts at 247°, and dissolves in alcohol and dilute acids yielding reddish-violet solutions; when heated at 210° for 8 hours with concentrated hydrochloric acid and a little glacial acetic acid, it is decomposed into α-naphthylamine and rosindone.

Isonaphthylrosinduline, $NPh{:}C_{10}H_5{<}{\genfrac{}{}{0pt}{}{N\overline{\quad}}{NPh}}{>}C_{10}H_6$, crystallises from toluene or xylene in deep-red plates, melts at 256°, and is, generally speaking, much more sparingly soluble than the isomeride, the solutions being of a more distinct red shade; it is decomposed by hydrochloric acid into aniline and an *oxyphenyldinaphthazine*, of the composition $C_{26}H_{16}N_2O$. The last named compound crystallises from cumene in shining, red, hexagonal plates, melts at 295°, and yields rose-red solutions which have a yellowish fluorescence; on the addition of an acid, the colour of the solutions changes to yellow, and the fluorescence becomes more marked. When distilled with zinc-dust in an atmosphere of hydrogen, it is converted into αβ-naphthazine.

If, in preparing phenylrosinduline ("rosinduline") by the method previously described (*loc. cit.*), the reaction takes place only slowly,

there is formed a considerable quantity of tri- and tetr-anilidonaphthalene; the two compounds can be separated by treatment with alcohol.

Trianilidonaphthalene [$(NHPh)_3 = 1:3:4$] is more readily soluble in alcohol than the tetranilido-derivative; it separates from a mixture of benzene and light petroleum in slender needles, melts at 148°, and has feeble basic properties. Its solutions show a blue fluorescence. On oxidation with mercuric oxide, it is converted into phenylrosinduline, a yellow compound melting at about 140°, probably anilidonaphthaquinonedianil, being formed as an intermediate product: this yellow substance is unstable, and on further oxidation it yields phenylrosinduline and trianilidonaphthalene.

The compound $C_{34}H_{28}N_4$ (m.p. 191°), formed in the preparation of anilidonaphthaquinoneanil (Abstr., 1888, 473), is identical with the tetranilidonaphthalene referred to above; it has the constitution [$(NHPh)_4 = 1:2:3:4$], and its solutions show a blue fluorescence.

A compound of the composition $C_{34}H_{26}N_4$, or $C_{34}H_{24}N_{44}$, is formed, together with anilidophenylrosinduline and a small quantity of a blue substance, probably dianilidonaphthaquinone, when tetranilidonaphthalene is boiled with yellow mercuric oxide (3—4 parts) in benzene solution for about half an hour; it separates from benzene in orange-yellow crystals and melts at 169°. On further oxidation, this yellow substance is converted mainly into anilidophenylrosinduline, and when heated with alcohol and concentrated sulphuric acid, it is decomposed into aniline and a compound, probably *dianilidonaphthaquinone*, which crystallises in blue needles.

Anilidophenylrosinduline, $C_{34}H_{24}N_4$, crystallises from benzene and alcohol in almost black plates, melts at 192°, and dissolves in concentrated sulphuric acid yielding a dark-green solution which turns red on diluting.

α-Naphthaquinonedianil, $C_{22}H_{16}N_2$, separates in crystals when the alcoholic solution obtained in the purification of phenylrosinduline (see above) is evaporated, and on further concentration, a brown substance melting at 171° is obtained. α-Naphthaquinonedianil crystallises in golden plates, melts at 187°, and is sparingly soluble in alcohol, but more readily in benzene; it resembles Bandrowski's diphenylparazophenylene in its properties.

The brown substance (m. p. 171°) is a molecular compound of naphthaquinonedianil and phenylrosinduline; it crystallises from benzene in shining plates, and is decomposed into its constituents by boiling alcohol or glacial acetic acid.

Diphenylparanaphthalenediamine, $C_{22}H_{18}N_2$ (*paradianilidonaphthalene*), is easily obtained by treating an alcoholic solution of α-naphthaquinonedianil with zinc-dust and glacial acetic acid; it crystallises from alcohol in colourless prisms, and melts at 144°.

The following azo-dyes employed in this investigation were prepared by the well-known method (Fischer and Hepp, Abstr., 1886, 1041).

Benzeneazoethyl-α-naphthylamine crystallises in red plates, or prisms, with a blue reflex, melts at 76°, and is readily soluble in alcohol and benzene; it dissolves in concentrated sulphuric acid and

in alcoholic hydrochloric acid, yielding reddish-violet solutions. The corresponding *phenyl*-derivative crystallises from alcohol in scarlet plates, melts at 151°, and is readily soluble in benzene, but only moderately easily in alcohol and sparingly in light petroleum; its solutions in concentrated sulphuric acid and alcoholic hydrochloric acid are of a beautiful blue colour. The corresponding *paratolyl*-derivative crystallises from alcohol in red plates with a blue reflex, melts at 144°, and resembles the phenyl-derivative in its behaviour with the solvents mentioned above.

Benzeneazo-α-dinaphthylamine melts at 128°, and is readily soluble in benzene and alcohol; it crystallises in short, orange-red prisms, and its solutions in concentrated acids are blue.

It has been previously shown by Nietzki and Schmidt (Abstr., 1888, 943) that the anilido-groups in dianilidoquinone occupy the para-position; since azophenine, on decomposition, yields aniline and the same dianilidoquinone, it must have the constitution

$$[(NPh)_2 : (NHPh)_2 = 1 : 4 : 2 : 5].$$

A further proof of this constitution is afforded by the fact that when symmetrical diamidoquinonediimide (Nietzki and Hagenback, Abstr., 1887, 476) is heated with aniline and aniline hydrochloride at 120°, considerable quantities of azophenine are formed.

Ditoluidotoluquinone, $C_{21}H_{20}N_2O_2$, prepared by boiling toluquinone with paratoluidine in alcoholic solution, crystallises in needles, and melts at 241°; it has probably the constitution

$$[O_2 : (NHC_7H_7)_2 : Me = 1 : 4 : 2 : 5 : 6].$$

Anilidotoluquinoneanil, $C_{19}H_{16}N_2O$, can be obtained by warming dianilidotoluquinoneanil with stannous chloride and glacial acetic acid until the solution becomes light-yellow; the filtered solution is diluted with water, the precipitated stannochloride dissolved in hot alcohol, decomposed with ammonia, and a stream of air passed through the filtered solution for several hours; it crystallises in red needles and melts at 151°.

Diphenyldiamidophenol hydrochloride, $C_{18}H_{16}N_2O,HCl$, is obtained when azophenine is reduced with tin and hydrochloric acid in acetic acid solution; it melts at 192° with decomposition. The *base* has probably the constitution $[(NHPh)_2 : OH = 1 : 3 : 4]$; it is very unstable, and on exposure to the air it is converted into anilidoquinoneanil.

Anilidoquinonedianil, $C_{24}H_{19}N_3$, is formed, together with various other products, when azophenine is heated at 160° with hydrochloric acid. It crystallises from alcohol in reddish-brown needles, melts at 229—230°, and dissolves in concentrated sulphuric acid yielding a blue solution which turns reddish-violet on diluting; on the addition of dilute acids to an alcoholic solution of the base, a reddish-violet solution is obtained, from which wool absorbs the colouring matter. When oxidised with potassium dichromate in acetic acid solution, it is converted into a bluish-violet induline, which probably corresponds with phenylrosinduline.

The paranitroso-derivative of methylxylidine, [$NHMe : Me_2 = 1 : 2 : 3$], is a beautiful green compound, and when heated with aniline and aniline hydrochloride, it yields a red induline. The indulines are, therefore, quinoneimide-derivatives (indamines), and the safranines possibly belong to the same class of compounds.

F. S. K.

Dextrococaïne. By A. Einhorn and A. Marquardt (*Ber.*, **23**, 979—988; compare this vol., 646).—The authors suggest that the "methylcocaïne" and "methylecgonine," prepared by C. Liebermann and F. Giesel (this vol. p. 647) from mother liquors obtained in the manufacture of cocaïne, are really dextrococaïne and dextroecgonine, which are formed by the action of an alkali on ecgonine during the evaporation of the mother liquors. For the better characterisation of the compounds, a number of new derivatives have been prepared. Dextrococaïne is best separated from ordinary cocaïne by means of the hydrochloride. The aurochloride of dextrococaïne, $C_{17}H_{21}NO_4,HAuCl_4$, is deposited from dilute alcohol in small, lustrous, yellow crystals melting at 149°. The platinochloride is very insoluble in water; it crystallises from dilute alcohol in pale-yellow, slender needles which melt at 218°. The hydrobromide is obtained from hot water in the form of long, prismatic needles. The iodide and nitrate crystallise in lustrous leaves; both they and the sulphate are sparingly soluble in water. Dextrococaïne is liberated from its salts by the action of sodium hydroxide; it is at first obtained as an oily liquid, which readily solidifies on adding a crystal of the substance; it crystallises in prisms melting at 43—45°. Benzoyl dextroecgonine hydrochloride, $C_{16}H_{19}NO_4,HCl$, is formed by heating dextrococaïne with water for 48 hours; the solution is freed from benzoic acid by shaking with ether, and the hydrochloride precipitated on addition of hydrochloric acid; it crystallises from water or alcohol in needles, or in short, broad, well developed crystals melting at 244—245°. The *aurochloride* of *ethyldextroecgonine*, $C_{11}H_{19}NO_3,HAuCl_4$, is deposited from dilute alcohol in orange-coloured crystals melting at 115°. The corresponding propyl compound has a similar appearance and melts at 132°. The isobutyl compound, $C_{14}H_{23}NO_3,HAuCl_4$, crystallises in orange-coloured, transparent leaves melting at 130°. The aurochloride of amyldextroecgonine is at first oily, after some time it solidifies and crystallises from absolute alcohol in yellow prisms melting at 152°. Ethereal salts of benzoyldextroecgonine are formed by the action of benzoic chloride on the above ethereal salts. *Ethylbenzoyldextroecgonine*, $C_5H_7NMe{\cdot}CH(OBz){\cdot}CH_2{\cdot}COOEt$, crystallises from ether in white prisms melting at about 57°. The hydrochloride is deposited from hot water or absolute alcohol in transparent triangular leaves melting at 215°. *Propylbenzoyldextroecgonine hydrochloride* crystallises from water or alcohol in white prisms melting at 220°. The hydrochlorides of the corresponding *isobutyl* and *amyl* compounds crystallise in interlaced needles melting at 201° and 217° respectively. *Amylbenzoyldextroecgonine hydrobromide* is comparatively insoluble in water, and crystallises in white leaves. The above salts are all dextro-rotatory, and have a physiological action similar to that of cocaïne. The authors have prepared

a fresh specimen of dextroecgonine, from methyldextroecgonine; on recrystallisation from methyl alcohol it melts at 257°, instead of 254°, as previously given; Liebermann and Giesel found 264° as the melting point of their "methylecgonine." J. B. T.

Determination of the Molecular Weights of Cholic Acid, Cholesterin and Hydrobilirubin, by Raoult's Method. By J. J. ABEL (*Monatsh.*, 11, 61—70).—The author contests the validity of the results given by Nencki and Rotschy (this vol., p. 76) on the ground that unsuitable solvents were used, and that bilirubin is itself changed on solution in acetic acid. Making use of pure phenol as a solvent, numbers are obtained closely approximating to those required by the formulæ, $C_{24}H_{40}O_5,C_6H_6O$; $C_{24}H_{40}O_5$; $C_{26}H_{43}\cdot OH$, and $C_{32}H_{40}N_4O_7$, for the phenate of cholic acid, cholic acid, cholesterin, and hydrobilirubin, respectively. G. T. M.

Physiological Chemistry.

Human Respiration. By W. MARCET (*Proc. Roy. Soc.*, **46**, 340—345).—Experiments were conducted on human beings at different altitudes on the Swiss mountains, and to avoid the disturbing influence of reduced atmospheric temperature, on the Peak of Teneriffe, in order to investigate the effect of varying pressure on the respiratory exchange of gases. It was found:—

1. That less air (reduced to 0° and 760 mm.) is breathed at high than at low altitudes for the formation of a given weight of carbonic anhydride in the body.

2. Incidentally, that the influence of food on the formation of carbonic anhydride is that the *maximum* expired occurs two or three hours after a meal, and the *minimum* before breakfast. This is merely confirmatory of older observations.

3. That the influence of food on the relation of the volumes of air breathed, and carbonic anhydride expired is marked, the volumes following the fluctuations of the carbonic anhydride, except four or five hours after a meal, when the carbonic anhydride expired falls proportionately faster than the volumes of air breathed.

4. That local atmospheric pressure has a marked influence on respiration, less air being inspired for the formation and emission of a given weight of carbonic anhydride under lower than under higher pressures; this influence varies in degree in different persons.

5. Digestion neutralises in a great measure the effects on any local change of atmospheric pressure on respiration. W. D. H.

Chemistry of the Urine of the Horse. By F. SMITH (*Proc. Roy. Soc.*, **46**, 328—340).—The chief object of this research was to ascertain the difference between the urine of work and the urine of

repose. In the first case the horse was worked for several days, and the urine of the next 24 hours collected. For this purpose a special stall was constructed with sloping sides, and a drain beneath. The urines examined numbered 96, complete analyses being made of 54. Normal urine was found to be invariably turbid, with a faint ammoniacal odour even when fresh, and always alkaline. Large quantities of mucus are often contained in the urine, particularly in that of mares. The following table shows the mean composition of the 24 hours' urine of horses at rest and at work.

	Rest.	Work.
Quantity	4935 c.c.	4474 c.c.
Specific gravity	1·036	1·036
	Grams.	Grams.
Total solids	230·0713	232·157
Organic solids	146·1649	152·190
Inorganic solids	83·9064	79·967
Urea	98·5110	
Ammonium carbonate as urea	13·1185	
Ammonia	2·516	5·3000
Benzoic acid	6·530	—
Hippuric acid	—	15·5870
Phosphoric anhydride	1·3000	1·8970
Sulphuric ,,	10·6468	15·2890
Other sulphur compounds	7·3166	7·6902
Chlorine	31·7119	21·9806
Calcium oxide	3·4367	1·9027
Magnesium oxide	2·9750	2·6300
Potassium oxide	36·5900	27·0600
Sodium ,,	2·5000	1·8400

J. W.

Chemistry of Vegetable Physiology and Agriculture.

Fermentation of Mannitol and Glycerol. By P. F. Frankland and J. J. Fox (*Proc. Roy. Soc.*, **46**, 345—357).—The micro-organism which produced the fermentation studied in this paper was obtained from sheep-dung by cultivation in glucose-peptone solution and afterwards in gelatin-peptone solution. The inoculations into the fermentable fluids were repeated until the organism was of perfectly uniform character. It is a bacillus whose appearance varies with the medium from which it is taken, being mostly paired (from liquids), or in long threads (from solid gelatin). No spores could be discovered in any of the cultivations.

In solutions containing 60 grams of mannitol or glycerol, 2 grams of peptone, 30 grams of calcium carbonate, and the necessary salts, fermentation went on briskly, more especially with the mannitol. The chief products of the fermentation were found to be ethyl alcohol and acetic acid: hence the authors propose the name *Bacillus ethaceticus*. Smaller quantities of formic and succinic acids were simultaneously formed. The proportion of alcohol to acetic acid in the mannitol fermentation is 1·63 : 1; in the glycerol fermentation it is 2·11 : 1. The action in both cases is incomplete. Solutions of glucose, cane-sugar, milk-sugar, starch, and calcium glycerate are fermented by the bacillus, but it has no action on dulcitol, erythritol, glycol, calcium lactate, tartrate, citrate, or glycollate. J. W.

Ferment-action of Bacteria. By T. L. BRUNTON and A. MACFADYEN (*Proc. Roy. Soc.*, **46**, 542—553).—This research was directed to determine in what way certain micro-organisms liquefy gelatin. The bacteria used were (1) Koch's comma spirillum (2) Finkler's comma spirillum, (3) a putrefactive micrococcus, (4) scurf bacillus, (5) Klein's "Welford" bacillus.

The liquefaction of the gelatin might be caused by the bacteria secreting some fluid which would simply dissolve it mechanically; or the solution might be effected by the gelatin being first altered chemically by a specific enzyme secreted by the bacteria. It was found that a temperature of 100° destroyed both the bacteria and the power of liquefaction, whilst a temperature of 50° destroyed neither. Exposure to temperatures between 60° and 75° killed the various organisms, but (in all cases except organism No. 3) did *not* affect the liquefying power, although active bacteria were proved to be absent. These circumstances seem to show that the bacteria which liquefy gelatin do so by means of a soluble enzyme. The authors succeeded in isolating this enzyme, and in demonstrating its peptonising action apart from the bacteria which produce it. They sum up their further results as follows:—

The most active enzyme is that formed in meat broth.

Acidity hinders, alkalinity favours its action.

The bacteria which form a peptonising enzyme on proteïd soil can also produce a diastatic enzyme on carbohydrate soil.

The diastatic enzyme is not so readily separated from the microbes which produce it, but where that has been accomplished its action on starch can still be demonstrated.

The diastatic enzyme has no effect on gelatin, and *vice versâ*.

The bacteria are capable of evincing an adaptiveness to the soil in which they grow.

The microbes are capable of digesting other similar bodies such as dextrose and muscle.

Fatty matter is not affected. J. W.

Gases contained in the Bladders of Fucus vesiculosus and Ozothellia nodosa. By N. WILLE (*Bied. Cent.*, 1890, 252–253).—The gas was collected under water, and was found to contain 35·0—37·57 per cent. of oxygen, but no carbonic anhydride under any conditions.

If the plants were dried for **10** hours in the air in the dark, the bladders contained 20·76—20·84 per cent. of oxygen. When the plants had been left in the dark for 12 hours, then the percentage was reduced to 2·68, whilst after 24 hours all the oxygen had disappeared. The gas, therefore, which is contained in those bladders which have been kept in water closely resembles in composition the air dissolved in sea water. E. W. P.

Rôle of Potassium in Plants. By R. LUPKE (*Ann. Agronom.*, **16**, 96; from *Landw. Jahrb.*, **17**, 887—913).—Growing the common haricot and the Spanish haricot in complete nutritive solutions, and also in the same solutions with potassium compounds only omitted, the author finds that the absence of potassium does not affect any one function or organ in particular, but that the general development of the plant is injured; all the organs are formed in turn, starch and other products of assimilation are produced, but the plants are smaller and fuller than those grown in the complete solutions.

As the cotyledons contain a store of potassium compounds, they should be removed as soon as practicable. The author's results are not in accord with those obtained by Noble some years ago on buckwheat, from which he concluded that without potassium no starch granules are formed. J. M. H. M.

Soluble Carbohydrates in Seeds of Legumes. By W. MAXWELL (*Amer. Chem. J.*, **12**, 265—269)—The author has previously discovered in the seeds of *Pisum sativum*, *Faba vulgaris*, and *Vicia sativa*, both cane-sugar and a substance ("galactan") which yields galactose when boiled with dilute mineral acids, and mucic acid when oxidised with strong nitric acid (this vol. p. 544).

He has recently detected the same substances, together with dextrin, in the seeds of *Phaseolus vulgaris*. The seed material was repeatedly extracted with 75 per cent. alcohol, and the extract boiled and saturated with strontium hydroxide. The strontium carbohydrate compounds thus formed were suspended in water and decomposed with carbonic anhydride, and the resulting solution evaporated to a syrup and extracted with alcohol. From the alcoholic extract, good crystals of cane-sugar were obtained; the residue, which was of a whitish-yellow colour, was dissolved in water, and the solution was purified from colouring matters, concentrated, and allowed to drop into absolute alcohol. A white, flake-like substance separated, which yielded galactose when boiled with dilute mineral acids, and mucic acid when heated with concentrated nitric acid; it was therefore a "galactan."

A quantitative estimation was made by extracting the seed material with water at 37—40°, inverting the solution with hydrochloric acid, and estimating the products of inversion gravimetrically. In this way it was found that the seeds of *Phaseolus vulgaris* contain 5·36 per cent. of soluble carbohydrates. Some of the seeds were then allowed to germinate, and when the radicle was 15 mm. long the development was arrested by drying the seeds at 100°, and an estimation of the soluble carbohydrates was made as before. Only 3·35 per cent. of

these was now found; hence 32 per cent. of the soluble carbohydrates in the mature seed had been used up by the embryo plant in the earliest stage of its development, during the short time necessary for the protrusion of the radicle, and before the appearance of the plumule. C. F. B.

Bark of Xanthoxylon Senegalense (Artar Root). By P. GIACOSA and M. SOAVE (*Gazzetta*, **19**, 303—333).—After a description of the known species of *Xanthoxylon* and of the literature of the subject, the following results are given of the examination of artar root, which presumably belongs to *X. Senegalense*, D.C.

The root is generally cylindrical, somewhat contorted, and covered with bark, the underlying wood is pale yellow with minute white spots, the annual rings are barely visible, the medullary rays are very fine and waving, and meet at the centre, where, however, there is no pith; the wood is very close, tough, hard, and heavy, and has neither taste nor smell. The bark is covered with waving, longitudinal furrows; in colour it is reddish-brown, with bright, yellow spots, or yellow with greyish patches; it has a peculiar aromatic odour, and a taste which is aromatic at first, then burning, and causes itching of the tongue.

The authors have previously mentioned (Abstr., 1888, 167) the occurrence in a specimen of this bark of a fixed oil, of a neutral, crystalline substance melting at about 120°, and of two alkaloïds, the more abundant of which is amorphous; the other, which occurs only in small quantity, crystallises in large, blood-red needles soluble in hot water.

To isolate the alkaloïds from fresh specimens of the bark, they are powdered, extracted with 94 per cent. alcohol, the extract condensed by distillation and evaporation to a syrupy consistency, made alkaline with soda, and extracted with ether; on treating the washed and concentrated ethereal solution with hydrochloric acid, it yields an abundant deposit of minute needles soluble in cold water. On the addition of ammonia or soda to the cold, aqueous solution of this hydrochloride, the base is precipitated as a light, amorphous, reddish-yellow, flocculent powder, the hot aqueous solution of which on evaporation does not yield the alkaloïd previously mentioned as crystallising in red needles. It would therefore appear that the latter is not a constant constituent of the bark. On purifying the alkaloïd by repeatedly combining it with hydrochloric acid, recrystallising, and decomposing the salt, the first portions of the hydrochloride which separate were found to be more insoluble than the succeeding portions. On collecting the former apart and treating them with alkalis, a perfectly white base is obtained. This appears to be crystallisable, and dissolves in acids forming pale-yellow salts; the *hydrochloride* dissolves with difficulty in water and alcohol, and crystallises out in pale, yellowish needles which, on heating at 200° darken, and melt at 270°.

Artarine is the principal alkaloïd in the bark of artar root, of which it forms 0·4 per cent. It is an amorphous, uncrystallisable, rose-grey powder which darkens a little on exposure to light; it turns brown

on heating to 210°, and melts with decomposition at 240°; when heated on platinum foil, it melts, decomposes, gives off white fumes having an odour of quinoline, chars, and is finally burnt away with difficulty, but without leaving any ash. It shows an alkaline reaction to damp reddened litmus paper, and is converted by acids into golden-yellow salts; it undergoes no change by prolonged keeping over sulphuric acid. It dissolves readily in ether, boiling amyl alcohol, and warm acetone, and also, when freshly precipitated, in warm methyl alcohol, only with difficulty in warm chloroform, and not at all in water or benzene. It is sparingly soluble in boiling 98 per cent. alcohol. The *hydrochloride*, $C_{21}H_{23}NO_4HCl$, may be purified by precipitating its alcoholic solution with an excess of ether. It crystallises in large, slender needles, occasionally forming tufts or nodules; it is blackened on heating to 60—70°, and melts at 189° with decomposition. It is freely soluble in methyl alcohol and in acetone, readily in warm chloroform and in amyl alcohol, moderately in warm alcohol, less so in warm water (0·514 per cent. at 14° C.), but is altogether insoluble in ether and in benzene. The presence of free acid considerably diminishes the solubility of the hydrochloride, and of all the other artarine salts. Solutions of the hydrochloride in water or alcohol are inactive to light. There are probably three hydrates of this compound, containing 2, 3, and 4 mols. H_2O respectively; the last of these is obtained by cooling an aqueous solution saturated in the cold; it melts at 194°. The *platinochloride* crystallises in slender, pale yellow needles which do not melt at 290°, and are insoluble in water and alcohol. The *hydriodide* is obtained by the action of potassium iodide on the hydrochloride; it crystallises in very slender, interlaced, yellow needles which dissolve freely in warm water and alcohol.

Another iodine-derivative, $C_{21}H_{23}NO_4HI_3$, is obtained by treating the cold alcoholic solution of artarine with a solution of iodine in potassium iodide; it forms aggregates of greenish-brown, microscopic needles which are insoluble in water, and only dissolve with difficulty in boiling absolute alcohol. The *sulphate* is a white powder, consisting of microscopic needles; it darkens on heating to 60—70°, and melts at 240°. The *nitrate*, obtained by adding potassium nitrate to an aqueous solution of the hydrochloride, is a thick, gelatinous, yellow mass containing a few microscopic crystals. It crystallises from alcohol in thin plates, a little longer and thinner than those of uric acid, and melts at 212°. The *phosphate* and *arsenate* crystallise in dirty yellow aggregates of microscopic prisms which are only very sparingly soluble in water; the *chromate* forms very long, reddish-yellow needles grouped in tufts; the *hydrobromide*, *molybdate*, *benzoate*, and *salicylate* are yellow, semi-crystalline powders; the *oxalate* and *tartrate* occur in hemispherical aggregates of needles; the *picrate* forms dendritic groups of very bright yellow needles.

The analyses of the compounds of artarine agree equally well with the formulæ $C_{21}H_{23}NO_4$ and $C_{20}H_{17}NO_4$ (berberine); other points of resemblance and distinction between artarine and berberine are as follows:—

Artarine forms yellow salts, the solubility of which is diminished

by the presence of acids; it also forms a periodide, and generally resembles berberine in its reactions. It differs from berberine in being colourless, uncrystallisable, and in the solubility, melting points, and crystalline character of its salts. It also dissolves in sulphuric acid without any discoloration, and is coloured blood-red by the action of potassium nitrate and concentrated sulphuric acid. The hydrochloride acquires by the action of chlorine-water at most a yellowish tinge which is dissipated on addition of ammonia. The double iodides of potassium and mercury or cadmium give yellowish, flocculent precipitates, and the iodide of potassium and bismuth gives a similar red precipitate, all of which are insoluble in excess of the reagent; phosphantimonic acid only occasions a slight turbidity which disappears in excess. If the formula $C_{21}H_{23}NO_4$ is adopted for artarine, its constitution is probably that of a methylhydroberberine.

The red alkaloïd, previously obtained from a specimen of the bark, crystallises in blood-red needles readily soluble in water, and forms yellow salts when heated with acids; the *hydrochloride* melts at 170°, the *sulphate* at 265°, and the *platinochloride* at 290°. Besides these alkaloïds, the authors previously isolated from the light petroleum extract of the bark a neutral, crystalline substance which is either identical with cubebin ($C_{10}H_{10}O_3$), or has the formula $C_{14}H_{14}O_4$. This substance crystallises in transparent, colourless prisms which melt at 123°, and dissolve readily in warm ether, chloroform, alcohol, and light petroleum, but are insoluble in water. Like cubebin, it is coloured dark-red by concentrated sulphuric acid; on the other hand, neither acetic nor pyrocatechuic acid was detected among the products of its fusion with potash. It is first coloured wine-red by concentrated sulphuric acid and then dissolved; in the presence of potassium chromate, it acquires a dull violet colour; it is not affected by potash or ammonia, even on heating. A mixture of sulphuric acid (4 vols.) and water (1 vol.) colours the crystals red and partially dissolves them in the cold; on gently warming, the liquid becomes violet, and the crystals are charred. If sulphuric acid is added to the chloroform solution of the substance, an intense purple-red coloration is produced at the points of junction of the two liquids.

A neutral nitrogenous substance of unknown composition has also been isolated; it forms pale-yellow crystals melting at 170°, and its alcoholic solution is coloured bright-green by ferric chloride.

S. B. A. A.

Analytical Chemistry.

Direct Estimation of Chlorine in Mixtures of Alkaline Chlorides and Iodides. By F. A. Gooch and F. W. Mar (*Amer. J. Sci.* [3], **39**, 293—302).—The authors have shown, in a great number

of experiments, that hydrochloric acid is stable under the conditions of the methods described below. In fact, no significant loss of chlorine by volatilisation or otherwise took place in the following cases, selected from the numerous examples given in the paper:—

1. When a solution containing 10 c.c. of sulphuric acid (1 to 1) and 1 gram of potassium chloride is concentrated from 400 c.c. to 300 c.c. by boiling for about half an hour.

2. Or when a solution containing 10 c.c. of sulphuric acid (1 to 1), 5 grams of iron-alum, and 5 c.c. of nitric acid, sp. gr. 1·40, is treated in a similar manner.

3. Or when a solution containing 10 c.c. of sulphuric acid (1 to 1), 2 grams of ferric sulphate, 5 c.c. of nitric acid, about 0·5 gram of potassium chloride, and 1 gram of potassium iodide. Or when nitrous fumes were substituted for the ferric sulphate.

On the other hand, iodine is fully expelled from hydriodic acid in the presence either of nitrous acid or ferric sulphate. It was found that without some agent to regenerate the ferrous sulphate produced in the reaction, an equilibrium was established before all the iodine was expelled, and the nitric acid was added for this purpose. The methods suggested are as follows:—

1. 10 c.c. of sulphuric acid (1 to 1), 2 grams of ferric sulphate (either as iron-alum or ferrous sulphate oxidised in concentrated solution by about 0·3 c.c. of nitric acid), and 3 c.c. of nitric acid are added to the solution of the alkaline iodide and chloride, diluted to 400 c.c., and the whole boiled until the steam ceases to colour red litmus paper greyish-blue, a reaction found by the authors to be characteristic for iodine and very delicate; the chlorine is then determined in the residue. In the second method, the iodine is expelled by passing in the gases evolved from 2 grams of sodium nitrite by the action of dilute sulphuric acid. A trap is used to prevent mechanical loss of liquid during boiling. D. A. L.

Estimation of Sulphur in Iron. By L. Blum (*Zeit. anal. Chem.*, **29**, 138—139).—Lucion having ascertained that the presence of bromine has no influence on the precipitation of barium sulphate, it might be supposed that when estimating sulphur in iron by dissolving in hydrochloric acid, and passing the gases through brominated hydrochloric acid, time would be saved without any compensating disadvantage by omitting the usual evaporation. Where hydrocarbons are evolved during solution, this is, however, not the case. There are formed oily brominated hydrocarbons, which, becoming entangled in the precipitated barium sulphate, retard the filtration so much that more time is consumed than would suffice for the evaporation. When evaporating the liquid to a small bulk, these brominated products remain adherent to the basin, and at the same time the further advantage is gained of expelling most of the hydrochloric acid, which, if retained, would lower the result by its solvent action on the barium sulphate. M. J. S.

Estimation of the Total Nitrogen in Manures. By E. Aubin and J. Quenot (*Bull. Soc. Chim.* [3], **3**, 322—326).—Several determina-

tions have been made by the authors, using different methods, and in all cases where nitrates are mixed with ammonium compounds Kjeldahl's method gives very low results. The estimation of the total nitrogen in such mixtures by treatment with sulphuric acid, phenylsulphuric acid, zinc, and mercury, gives numbers which are approximately correct. The authors consider that the treatment of manures with ferrous sulphate in order to destroy the nitrates (which are determined in a further sample by Schloesing's method), before applying Kjeldahl's method, is satisfactory, except that no separation of organic nitrogen as existing apart from ammonium salts is possible. They have devised the following process, in which use is made of the fact that tannic acid precipitates the albumin contained in the manure, and thus renders the organic nitrogen insoluble:—1 gram of the manure is placed on a small filter, and is exhausted with 30—40 c.c. of a 2 per cent. tannin solution. The nitrogen contained in the residue is estimated by Kjeldahl's method, and is the organic nitrogen, whilst the filtrate similarly treated gives that existing as ammonium salts; the nitrogen present as nitric acid being determined by Schloesing's method. In the case of manures containing ammonium-magnesium phosphate, 1 gram of manure should be digested with 0·5 gram of tannin in 150 c.c. of carbonic acid water for 15 hours; the residue and filtrate are to be treated as above described. The results published point to the accuracy of the method.

T. G. N.

Test for Nitrous Compounds in Sulphuric Acid. By J. H. WILSON (*J. Pharm. Trans.* [3], **20**, 541).—Resorcinol is a delicate and convenient test for nitrous compounds in sulphuric acid, as it immediately produces a more or less intense yellow colour, according to the quantity of these compounds present in the acid. 1 c.c. of the acid is added to 5 c.c. of water, allowed to cool, and a minute portion of resorcinol dropped in, and stirred with it until dissolved. The test can be made a quantitative one by using Nesslerising glasses as in Wanklyn's method of estimating ammonia.

R. R.

Use of the Induction Spark for Detecting Traces of Arsenic. By N. KLOBUKOW (*Zeit. anal. Chem.*, **29**, 129—133).—Ogier has shown that hydrogen arsenide is gradually but completely decomposed into its elements at ordinary temperatures by the induction spark. If, therefore, the gaseous mixture from a Marsh's apparatus is passed slowly through a narrow tube, into which are inserted from the opposite ends two platinum wires, forming the terminals of an induction coil, the whole of the arsenic will be deposited on the glass in the immediate neighbourhood of the sparks; even so small a quantity as 0·01 milligram forming a distinct metallic mirror. The tube should be about 0·7 to 0·8 mm. in internal diameter, the wires 0·5 to 0·6 mm. diameter and 3 to 4 mm. apart; about 10—15 c.c. of gas may be passed per minute, and a small induction coil capable of giving sparks of 16—17 mm. with the current of two large Bunsen cells will suffice.

M. J. S.

Estimation of Arsenic. By R. C. CANBY (*Zeit. anal. Chem.*, **29**, 187; from *Journ. Analyt. Chem.*, **2**, 411).—About a gram of the pulverised ore is mixed in a porcelain crucible with 4 or 5 parts of sodium carbonate and the same weight of potassium nitrate, and heated gradually to fusion. After 3 to 5 minutes it is cooled, dissolved in warm water, filtered, and the residue washed with warm water. The filtrate is acidified with nitric acid and boiled, then cooled and mixed with an excess of levigated zinc oxide. Should this produce a precipitate of silica or alumina, it is filtered off, then a further quantity of zinc oxide is added, and the arsenic acid precipitated by a small excess of silver nitrate whilst stirring vigorously. The washed precipitate, consisting of silver arsenate and the excess of zinc oxide, is dissolved in hot, dilute nitric acid, the solution cooled, mixed with a little ferric sulphate, and titrated with ammonium thiocyanate. M. J. S.

Estimation of Carbon in Graphite. By J. WIDMER (*Zeit. anal. Chem.*, **29**, 160—163).—The defect pointed out by Cross and Bevan (Trans., 1888, 889) in the chromic acid oxidation process, namely, that part of the carbon is oxidised only to monoxide, is found to exist also in the oxidation of graphite by the same reagent, about 5 per cent. of the carbon being evolved as monoxide, but in this case the remedy suggested by them is inapplicable, since with the larger excess of chromic acid, greater strength of sulphuric acid, and higher temperature requisite for oxidising graphite, an evolution of oxygen cannot be prevented. The author finds it necessary to pass the gases over heated copper oxide before collecting and weighing the carbonic anhydride. The apparatus used consists of a round-bottomed flask of 200—300 c.c. capacity, with a long neck placed obliquely, so that the acid mixture may not spurt up to the rubber stopper, then a Liebig's condenser and a U-tube containing glass beads moistened with strong sulphuric acid. This is followed by a large U-tube containing calcium chloride, and pumice soaked in cupric sulphate, then a combustion tube 40 cm. long, containing granular cupric oxide, of which at least 15 cm. should be heated to redness. The gases then pass through another calcium chloride tube, and then into the absorbing tubes containing soda lime and calcium chloride. A guard tube and an aspirator of 6—8 litres capacity complete the apparatus. Air is admitted to the flask through potash, soda lime, and a cotton-wool filter. The author's experiments were made with about 0·3 gram of graphite, 10 grams of chromic acid, and 65 c.c. of sulphuric acid, which should not be of greater strength than 2 vols. of concentrated acid to 1 vol. of water. The mixture in the flask is to be heated to gentle boiling, whilst about 6 litres of air is slowly aspirated through the apparatus. M. J. S.

Estimation of Graphite in Minerals. By J. B. MACKINTOSH (*Zeit. anal. Chem.*, **29**, 205).—A few fragments of potash are heated to tranquil fusion in a silver crucible. The weighed substance, which should not be very finely powdered, is added, and stirred from time to time with a silver wire, the temperature being somewhat

raised, and the fusion continued until sandy particles are no longer perceptible. After cooling, the mass is digested with cold water. The graphite will be left in the insoluble residue, together with lime, magnesia, ferric oxide, &c., whilst other carbonaceous substances will have been destroyed. The residue is collected in a Gooch crucible, washed with water, and treated with dilute hydrochloric acid, then with ammonia, and finally washed, by which means all foreign matter is removed, and the pure graphite remains.

M. J. S.

Volumetric Estimation of Carbon in Iron. By J. Wiborgh (*Zeit. anal. Chem.*, **29**, 198—204; from *Berg. Hütt. Zeit.*, **46**, 223, 233).—The carbon in iron can be completely oxidised to carbonic anhydride if the iron is treated with a sufficiently concentrated solution of chromic acid in sulphuric acid, at a temperature near its boiling point. At lower temperatures, hydrocarbons are evolved. If, however, the iron is first treated with a neutral solution of cupric sulphate (which, except in rare cases, can be done without the loss of more than traces of hydrocarbons), the copper protects the iron from the action of the acid mixture until the temperature is reached at which oxidation to carbonic anhydride will occur. The iron must be in filings or borings fine enough to pass through holes 1·5 mm. in diameter. About 0·2 gram of wrought iron or of steel, or 0·1 gram of cast iron should be used. It is placed in a vessel like a test-tube and treated with 4 c.c. of a saturated solution of cupric sulphate. After stirring for 10 minutes (or only three or four if any smell of carburetted hydrogen is observed), 1·2 gram of chromic acid is added and well mixed in, keeping the mixture cool by immersing the cylinder in cold water. The tube is then closed with a rubber stopper carrying a stopcock funnel and a narrow tube for conveying the gases into a gas-burette. A special form of gas-burette is described, which has a total capacity of about 60 c.c., and at its lower part consists of a tube about 200 mm. long, 9 mm. diameter, and graduated in twentieths of a c.c. To the contents of the reaction tube, 8 c.c. of sulphuric acid of sp. gr. 1·7 is now added, and the mixture boiled for 10 minutes, after which the whole of the gaseous contents are driven over into the burette by filling the cylinder with water through the stopcock funnel. The total volume is read, and the carbonic anhydride is then absorbed by introducing potash solution into the burette through a funnel at the top. It is stated that in consequence of a small loss of carbonic anhydride by absorption in the water with which the burette is filled, 1 c.c. measured at 18°, is equal to 0·29 per cent. of carbon when 0·2 gram of iron is used, and that a variation of 2° or 3° may be neglected. M. J. S.

Separation of Barium and Strontium. By R. Fresenius (*Zeit. anal. Chem.*, **29**, 143—160; continued from this vol., p. 826). —In connection with the separation by means of hydrofluosilicic acid, the following points have been investigated :—

Solubility of Barium and Strontium Silicofluorides.

Percentage composition of solvent by volume	water	100	50	74·1	70·8	77·95	73	97·09	75	95·24
	alcohol (96 per cent.)	0	50	25	25	20	25	0	25	0
	hydrochloric acid (20 p. c.)	0	0	0·9	4·2	0·9	0·9	1·25	0	2·04
	hydrofluosilicic acid (3 7 p. c.) .	0	0	0	0	1·15	1·1	1·66	0	2·72
1 part of barium silicofluoride requires ...		—	37219	5263	2860	39061	70679	3247	16914	—
1 part of strontium silicofluoride requires		31·06	1529	82·93	50·9	55·0	82·97	—	147·4	7·3

Barium silicofluoride dried at 100° retains a variable quantity of water (0·78 to 1·16 per cent. have been observed), the amount of which more than compensates for the loss due to its solubility, so that when the silicofluoride is dried at 100° and weighed, the results are high, but when it is converted into sulphate, a low yield is obtained. By using a considerable excess of hydrofluosilicic acid (which reduces the solubility of the precipitate) and converting into sulphate for weighing, passably good results may be obtained. On attempting to separate barium from strontium by precipitation with hydrofluosilicic acid in presence of alcohol, the separation is incomplete, whichever metal predominates; strontium is retained by the precipitate, and barium passes into the filtrate. The error due to this cause can be greatly diminished by conducting the process as follows. The solution containing the barium and strontium is mixed with excess of hydrofluosilicic acid, stirred, and allowed to remain for 30 minutes, after which alcohol (4 vols. to 10 vols. of the solution) is added, and the mixture again allowed to repose for two hours. The precipitate is first washed with dilute alcohol (1 : 1), and then several times with small quantities of cold water. The aqueous washings are concentrated to a small bulk, mixed with a few drops of hydrofluosilicic acid and $\frac{1}{3}$ volume of alcohol, and the small precipitate obtained filtered off after two hours. The filtrates are all united, and the strontium precipitated by sulphuric acid and alcohol. For a more perfect separation, the following method is recommended:—The aqueous solution of the barium and strontium chlorides is precipitated with hydrofluosilicic acid without addition of alcohol, and the precipitate is washed with cold water. Only when strontium largely predominates in the mixture will the precipitate retain traces of it. The filtrate and washings are measured, and a quantity of N/2 sulphuric acid added sufficient to precipitate five or six times the quantity of barium corresponding with the solubility of barium silicofluoride. The small precipitate obtained will contain all the barium together with a little strontium. It is to be fused with sodium car-

bonate, the barium and strontium carbonates washed with ammoniacal water, converted into chlorides, and separated by hydrofluosilicic acid in presence of alcohol. Although this last separation is a somewhat imperfect one, yet, as the errors fall upon only a very small part of the original mixture, they may safely be neglected. Test analyses gave unexceptionable results.

In the above process it is necessary to ascertain the strength of the hydrofluosilicic acid by titrating it with soda; using phenolphthaleïn or litmus (with heating), 1 equivalent of hydrofluosilicic acid requires 3 equivalents of soda, but if ethyl-orange is used, only 1 equivalent of soda is required. The total amount of the bases to be separated is then regarded as baryta, and a few grams more than the corresponding quantity of hydrofluosilicic acid is added. The dilution must be such that if the bases consisted entirely of strontia, the whole would remain dissolved. For 1 gram there must therefore be about 150 c.c. when alcohol is not used, and 200 to 250 c.c. when $\frac{1}{3}$ or $\frac{1}{4}$ of the liquid consists of alcohol. Free acids must be completely absent. M. J. S.

Volumetric Analysis of Copper. By R. A. FESSENDEN (*Chem. News*, **61**, 183).—The author finds that the titration of copper with potassium cyanide can be conducted more quickly and accurately by neutralising with sodium carbonate instead of ammonia, and taking care to have sufficient nitric acid present; neither the presence of sulphuric acid nor varying the proportions of the reagents affects the results. D. A. L.

Detection of Mercury in Organic Liquids. By E. BRUGNATELLI (*Gazzetta*, **19**, 418—422).—50—100 c.c. of the liquid is acidified with a few drops of hydrochloric acid, heated with purified copper foil or wire to 50—60°, agitated for five minutes, the copper removed, washed with distilled water, transferred to a glass vessel, and a porcelain lid on which a drop of a dilute solution of gold chloride is spread is placed over or beside it, the whole is covered with a watch glass, and heated on the water-bath. The gold chloride is reduced by the mercurial fumes, and the metal is deposited on the porcelain lid as a bluish-violet film or stain. One-tenth of a milligram of mercury may in this way be detected in a litre of liquid.

The precautions to be observed are to use only copper which has been calcined and then reduced in hydrogen, and to render the porcelain lid chemically free from organic matter. Both copper and lid must not be handled otherwise than with perfectly clean forceps. S. B. A. A.

Combustion with Lead Chromate. By R. DE ROODE (*Amer. Chem. J.*, **12**, 226—228).—A mixture of 4 parts of finely divided lead chromate and 1 part of red lead is washed thoroughly and dried by the pump; the moist mass is then divided into small lumps and ignited in a porcelain crucible, and the lumps are finally broken up in a mortar to the size of grains of wheat. In the fore part of the combustion-tube is placed a roll of reduced copper gauze; this the author finds to be necessary whether the substance to be analysed contains

nitrogen or not. Then comes a plug of asbestos, then the coarse grains of the above preparation filling about two-thirds of the rest of the tube, then another asbestos plug, then a mixture of the substance to be analysed with some of the above preparation in a state of fine powder, and finally some more of this latter in coarse grains. The fore part of the tube is connected with the calcium chloride tube and potash bulbs, the other end with an apparatus furnishing pure dried air; and the combustion is carried out as usual. The mixture of lead chromate and oxide does not fuse at a red heat, and the same tube may be used over and over again, except that the finely powdered portion of the mixture must be renewed every time, and occasionally the reduced copper gauze. C. F. B.

Estimation of Ethyl Nitrite in Spirit of Nitrous Ether. By J. C. Thresh (*J. Pharm. Trans.* [3], **20**, 752—755).—In estimating nitrous compounds by titration of the iodine they liberate from hydriodic acid, the author prevents access of air by conducting the operations in an atmosphere of coal-gas, instead of using a vacuous flask, as Dunstan and Dymond do in the same process. The apparatus is simply a bottle or flask of 350 c.c. capacity, provided with a rubber stopper having two openings with tube connections for the introduction of the gas, and the burettes, &c. Certain precautions are pointed out, such as the avoidance of violent agitation of the liquid, previous boiling of the water to expel air, and, if necessary, making a slight allowance for the oxygen contained in the volumetric solution. The small quantity of oxygen usually contained in coal-gas is eliminated from the atmosphere in the flask before the introduction of the spirit to be tested, by adding 2 or 3 c.c. of spirit of nitre, passing a current of coal-gas, and allowing the apparatus to stand a short time and then adding enough thiosulphate to destroy the colour. The measured quantity of spirit of nitre is then added and titrated. Tables are given to show the accuracy of the results, which are always slightly higher than those given by Allen's method with the nitrometer.

R. R.

Reagents for α- and β-Naphthol. By — Yvon (*J. Pharm.* [5], **21**, 465—468).—10 c.c. of an aqueous solution of β-naphthol containing 0·2 gram per litre when mixed with 2 c.c. of 90 per cent. alcohol, 2 c.c. of nitric acid, and 10 drops of mercuric nitrate solution (Codex), gives an intense orange-red colour, unaltered on boiling, which imparts a rose-red tint to gun-cotton. Sulphurous acid does not destroy the colour, or but slowly; the mixture passes to rose colour, becomes turbid, and at length gives a yellow or black deposit of mercury oxide. Chloroform takes up the original colouring matter and becomes intense ruby-red, at length turning greenish-yellow. Under the same conditions ether becomes yellow. If instead of the mercuric nitrate and nitric acid three drops of a saturated potassium nitrite solution and ten drops of pure sulphuric acid are added, an intense violet-red coloration results, which is destroyed by sulphurous acid and becomes greenish-yellow. Chloroform becomes greenish-yellow, and ether yellow. Gun-cotton assumes a wine-red tint. α-Naphthol under like conditions gives with the mercuric nitrate mixture an orange-yellow

colour, not changed on heating. Chloroform agitated with this takes an orange-yellow colour, and ether a somewhat greenish-yellow; sulphurous acid produces a brick-red precipitate, which settles and leaves a partly decolorised but still yellow liquid; gun-cotton is tinted yellow. With the potassium nitrite mixture, a reddish-brown colour is produced passing to wine-brown on boiling. Chloroform agitated with the mixture takes a greenish-brown colour, and ether becomes slightly greenish-yellow, while the aqueous solution assumes a clear, rose-red tint. The coloration is rapidly destroyed by sulphurous acid, and passes to a dirty green. Gun-cotton is tinted a dirty yellow. These reactions can be employed in studying the elimination of naphthol by the urine. With this object, the urine is shaken up with ether, this is decanted, evaporated to dryness, and the residue is taken up with 2 c.c. of alcohol; 10 c.c. of water is added, and the tests are applied as above. J. T.

Estimation of Starch in Grain. By Z. v. MILKOWSKI (*Zeit. anal. Chem.*, **29**, 134—136).—The author has made numerous estimations of starch in barley by the methods of Asbóth and Märcker respectively, and concludes from the agreement between the results that both methods are entitled to confidence. In carrying out Asbóth's process, the flour was freed from fat by ether, or carbon bisulphide, and quantities of 1—2 gram, thoroughly pulverised, were taken. In Märcker's method, 3 grams of the finely powdered substance is gelatinised by heating with 50 c.c. of water in a boiling water-bath, then cooled to 70° and mixed with 5 c.c. of malt extract (100 grams of malt to 500 c.c. of water), and kept at 70° for some minutes for the liquefaction of the starch paste. To prevent darkening, the solution is acidified with 1 per cent. of tartaric acid. The liquid is now exposed to a pressure of 3 atmospheres. After cooling, 5 c.c. of malt extract is again added, and the mixture is once more warmed to 70° and kept at that temperature for 20 minutes. This completes the solution of the starch. A portion of the filtered liquid is now inverted with hydrochloric acid of 1·125 sp. gr., and finally the sugar is estimated by Fehling's solution, using either Allihn's gravimetric, or Soxhlet's volumetric, process. A deduction must be made for the 10 c.c. of malt extract added. M. J. S.

Discrimination of Jute Fibres from those of Flax and Hemp. By W. LENZ (*Zeit. anal. Chem.*, **29**, 133—134).—A fragment of the fabric is warmed with ordinary nitric acid and a trace of potassium chlorate, then washed with water, and warmed with dilute potash solution until the acid in the fibres is neutralised. The alkaline liquid is poured off and the fibres shaken vigorously with pure water. The fibres now diffuse themselves uniformly through the water, and in this condition are poured upon a glass slip and allowed to dry in a horizontal position. After adding a drop of glycerol, a cover glass is placed over the specimen, and when the glycerol has thoroughly penetrated the fibres, they are examined under the microscope. The jute fibres now exhibit with great distinctness the irregular thickness of the cell walls. If placed between the crossed Nicols, the flax and

hemp fibres show an extremely rich play of colour, whilst those of jute are uniformly bluish or yellowish, except where they happen to touch or cross one another, and even there the colour is less bright.

M. J. S.

Milk Analysis. By F. WALLS (*Chem. News*, **61**, 162).—The author finds it advantageous to replace the paper coil of the Adam's process by a bottomless test-tube, filled about one-third with freshly ignited asbestos. The upper opening may be closed with a cork fitted with a tube in connection with an aspirator, by which means the evaporation to dryness is greatly aided.

D. A. L.

Melting and Solidifying Points of Fats and of their Mixtures. By A. TERREIL (*Bull. Soc. Chim.* [3], **3**, 195—200).—The author considers that the solidifying point of a fat, as determined by the slow cooling of the melted substance on an enlarged thermometer bulb, should alone be recognised as a test of purity. This point is always from 4—5° below the melting point. He describes a thermometer adapted for this purpose, and gives a very complete table, which indicates the melting, clouding, and solidifying temperatures of the principal fats, and of their mixtures with other fatty substances.

T. G. N.

Analysis of Fats. By H. NOERDLINGER (*Zeit. anal. Chem.*, **29**, 6—13).—Attention is called to the importance of estimating the free fatty acids in oils, and in articles of food containing fatty constituents, as the freshness and quality of the substances are closely connected with the amount of free acid present. To secure uniformity, all results are stated as oleic acid. The following table shows the mean percentage of fat and free fatty acid in various seeds:—

	100 parts of seed contain		100 parts of fat contain free fatty acid.
	Free fatty acid.	Total fat.	
Turnip (*Brassica rapa*)	0·42	37·75	1·10
Colza (*B. campestris*)	0·32	41·22	0·77
Poppy (*Papaver somniferum*)	3·20	46·90	6·66
Earth-nut (*Arachis hypogæa*)			
a. Seed	1·91	46·09	4·15
b. Husk	1·91	4·43	43·10
Sesame (*Sesamum orientale*)	2·21	51·59	4·59
Castor (*Ricinus communis*)	1·21	46·32	2·52
Palm kernel (*Elais guinensis*)	4·19	49·16	8·53
Cocoa-nut (*Cocos nucifera*)	2·98	67·40	4·42

In pressing oil from seeds, the free fatty acids are not obtained *pari passu* with the neutral oils. For instance, 100 parts of poppy seed containing 46·9 parts of oil, of which 3·2 parts are free acid, will yield on first pressure 39 parts of oil containing 0·75 part of acid, on second pressure 2·5 parts of oil containing 0·38 part of acid, and will

leave in the cake 5·4 parts of oil, of which 2·07 are acid. The following table gives the oil and free acid in the residue left after pressing:—

	100 parts of cake contain						100 parts of the oil contain free fatty acid.		
	Free fatty acid.			Total fat.					
	Max.	Min.	Mean.	Max.	Min.	Mean.	Max.	Min.	Mean.
Rape cake	1·02	0·72	0·93	9·70	7·67	8·81	13·23	8·39	10·55
Poppy cake....	6·86	3·72	5·66	10·34	8·92	9·63	70·70	43·70	58·89
Earth-nut cake .	4·92	0·37	1·42	12·47	5·70	7·65	39·42	6·45	18·62
Sesame cake	7·80	2·66	6·15	21·90	11·20	15·44	58·62	20·24	40·29
Palm kernel cake	3·16	0·62	1·47	14·70	8·00	10·39	26·21	6·28	14·28
Extracted palm kernel meal...	—	—	1·55	—	—	18·68	—	—	8·29
Cocoa-nut cake..	1·63	0·91	1·31	16·11	10·10	13·11	13·88	7·27	10·51
Linseed cake....	1·06	0·43	0·75	10·80	6·82	8·81	15·50	4·00	9·75
Colza cake	1·74	0·68	1·27	8·17	4·80	6·53	28·72	8·33	20·07

The fact that in the extracted palm-kernel meal the residual oil contains the same percentage of acid as the oil in the original seed, shows that the solvents used (carbon bisulphide or petroleum) exert no selective action, and this may serve as a means of distinguishing extracted from expressed oil, as well as the residual cake from the respective methods. In various specimens of deteriorated oil-cake (palm kernel and cocoa-nut), the free acid in the residual oil ranged from 17 per cent. to the whole. M. J. S.

Detection of Cotton-seed Oil in Fats and in Olive Oil. By T. Leone (*Gazzetta*, **19**, 355—357).—The author finds that 75 per cent. of the samples of lard analysed by him contain cotton-seed oil. This substance may be detected by adding a few c.c. of a 1 per cent. solution of silver nitrate in alcohol acidified with 0·5 per cent. of nitric acid, to a few c.c. of the lard, and heating on the water-bath for 5 to 6 minutes. If cotton-seed oil is present, a brownish-yellow ring is formed at the surface of separation of the two liquids. This reaction is sufficiently delicate to detect the presence of 5 per cent. of cotton-seed oil in lard. It may be used for the detection of this impurity in olive oil, in which case it is, however, preferable to heat for 10—12 minutes. The yellow ring is not given by other oils, although occasionally a white ring is observed which changes to green on prolonged heating. S. B. A. A.

Note.—This test has since been superseded by better methods.

Estimation of Fat in Feeding Stuffs. By H. J. Patterson (*Amer. Chem. J.*, **12**, 261—265).—The use of animal charcoal is recommended to remove the water, soluble acids, &c., with which

the fats and oils obtained by extracting food stuffs with ether are more or less contaminated. In the percolator-tube of the extraction apparatus is placed first some pure animal charcoal, then a plug of cotton, then the substance to be extracted, and finally another plug of cotton. The latter plug distributes the ether in a uniform stream over the substance, and prevents the latter from crawling up the sides of the percolator; the first plug prevents the fat coming in contact with the charcoal before it is thoroughly in solution. With grains and meals, 1 gram of charcoal per gram of substance was used; with hay, fodders, &c., 2 grams. A set of experiments made with pure fats showed that there was no loss in passing ethereal solutions of these through animal charcoal, and another set made upon various food stuffs showed that the method always gave lower, often much lower, results than the usual method, and that therefore the oil obtained by the latter method is more or less impure. C. F. B

Estimation of Urea. By D. B. DOTT (*J. Pharm. Trans.* [3], **20**, 793).—In the estimation of urea by measurement of the volume of nitrogen evolved, calcium hypochlorite is as trustworthy a reagent as sodium hypobromite, and the former has the advantages of being more easily and conveniently prepared (by mixing 1 part of bleaching powder with 3 parts of water and filtering); of keeping for a considerable time, whilst the hypobromite rapidly deteriorates; and of being cheaper. R. R.

Volumetric Estimation of Tannin. By E. GUENEZ (*Compt. rend.*, **110**, 532—534).—When a solution of tannin is added to a boiling solution of tartar emetic mixed with certain coal tar colours, antimony tannate is precipitated, and carries down the colouring matter in the form of a true "lake." After a sufficient quantity of the tannin has been added, the liquid above the precipitate becomes quite colourless. Dilution of the solutions is without influence on the results, and a given quantity of antimony tannate always carries down the same quantity of colouring matter. Gallic acid also does not interfere.

Green dyes only are suitable, and Poirrier's green 4JE. gives very good results. 12 grams of tartar emetic and 1 gram of the dye are dissolved separately in water, and the solutions are mixed, filtered, and made up to 1000 c.c. This liquid is standardised by means of a solution of 5 to 6 grams of pure tannin in a litre of water mixed with a small quantity of thymol to prevent the development of mould.

A measured volume of the antimony solution is heated to boiling, and the tannin solution is added from a burette, at first in cubic centimetres at a time, and afterwards in drops, the liquid being boiled after each addition. The precipitate settles readily, and the end reaction is easily perceived.

If the solution is standardised with tannin from nut-galls, the results with all other extracts will be expressed in terms of this tannin. C. H. B.

Estimation of the Indigo in Dyed Fabrics. By A. RENARD (*Zeit. anal. Chem.*, **29**, 97; from *Mon. sci.*, **28**, 1444).—A solution of

sodium hyposulphite is prepared from one of sodium hydrogen sulphite of 35° Baumé, and 100 c.c. of it is mixed with 100 c.c. of milk of lime and 2 litres of water. Of this mixture, 200 c.c. is placed in a flask containing 10 grams of the dyed stuff, and warmed to 60—70° while passing a stream of coal gas. When the decolorisation is complete, the liquid is rapidly poured into a graduated cylinder, and, after cooling, is measured. The indigotin is then precipitated by hydrochloric acid, and after 12 hours' subsidence is collected on an asbestos filter, washed, dried, dissolved in 10 c.c. of fuming sulphuric acid, and titrated according to Müller's method (*Jahresb.*, 1874, 1019). M. J. S.

Reaction of Cholesterin. By — OBERMÜLLER (*Chem. Centr.*, 1890, i, 299—300; from *Arch. Physiol.*, 1889, 556—558).—Several of the compounds which cholesterin forms with organic and inorganic substances assume characteristic colours during cooling after being melted.

In the *propionate* the author has found a most characteristic and delicate means of detecting cholesterin, the colours which this substance assumes during the process of cooling being intense and distinct, and also are of longer duration than are many of the other cholesterin reactions.

10 grams of cholesterin is melted with 5 grams of propionic anhydride. The *propionate*, $C_2H_5{\cdot}COOC_{27}H_{45}$, crystallises in rhombic plates resembling cholesterin, and as the substance cools it gradually assumes the colours violet, blue, green, dark-green, orange, carmine, and finally copper-red. The deep blue and the green especially remain a considerable time. If suddenly cooled, the substance assumes the copper-red colour, which also remains a considerable time. If the substance in a flask be melted in warm glycerol solution at 98°, it assumes the blue colour. The colours are seen by reflected light; if viewed by transmitted light, the complementary colours are observed. Examined under the polarising microscope with transmitted light, the melted substance becomes first blue-green, then greyish-blue, followed by light-blue, a constant motion being observed; then suddenly it remains stationary, and groups of crystals in spheroid form appear, which, under crossed Nicols, show the black cross indicative of doubly refracting crystals. The mass becomes again set in motion, the crosses vanish and it assumes a wine-yellow colour mixed with red, then a violet, blue, light-green, dark-green colour is observed; the last suddenly disappears, and again aggregates of doubly refractive crystals appear which are much larger than the first.

In applying the test for the detection of cholesterin, the latter is separated as far as possible from other substances; a small quantity is then melted carefully with two or three drops of propionic anhydride. By suddenly cooling, a lustrous fatty mass is obtained, and if a small portion of this is melted on a glass rod and held against a dark background, the colour reactions are readily observed. J. W. L.

General and Physical Chemistry.

Effect of the Spectrum on the Haloïd Salts of Silver. By W. DE W. ABNEY and G. S. EDWARDS (*Proc. Roy. Soc.*, **47**, 249—275). —This paper gives an account of the method employed to measure the relative sensitiveness of a photographic plate to the different parts of the spectrum. The density of the deposit at any spot is ascertained by allowing a beam from a constant light-source to pass through the plate, and cast the shadow of a rod on a screen in such a manner that it falls exactly alongside another shadow of the same rod cast by a second constant lamp. The intensity of the beam which has passed through the plate is reduced by varying the size of sectors cut out of a rotating disc placed in its path, until the two shadows are of the same degree of darkness. From the time of exposure of the different parts of the plate, and the opening of the sectors, the relative sensitiveness can be calculated. Collodion and gelatin plates of the different silver haloïds, both separate and mixed, were examined, and the results are given in numerous tables and curves. Plates dyed with cyanin and erythrosin were also investigated. J. W.

Polarisation of Electrodes. By L. POINCARÉ (*Compt. rend.*, **110**, 950—951).—The maximum polarisation which metallic plates can acquire when plunged into an electrolyte varies with the temperature, and, if the electrolyte is a fused salt, can be followed through a somewhat wide interval. Maximum polarisation is attained most quickly when the electrodes are short, slender wires.

With silver electrodes in fused sodium nitrate, the E.M.F. of polarisation is 0·33 volt at 330°, but it falls to 0·1 volt at 440°, and tends towards zero as the temperature rises to 470°, the point at which the salt begins to decompose. Similar experiments with potassium and ammonium nitrates, potassium and sodium chlorates, and mixtures of nitrates which decompose at different temperatures prove that the polarisation of silver electrodes is nil at the temperature at which the electrolyte decomposes. The same result is obtained with electrodes of iron or of gold. These results are analogous to Bouty's observation that in concentrated nitric acid, which is easily decomposed, the polarisation of platinum electrodes is very slight.

If it is assumed that the maximum polarisation is equivalent to or higher than the energy used up in the electrolytic decomposition, it follows that a rise of temperature tends to dissociate the electrolyte into its ions, and if the actual products of decomposition are not the ions, they are produced from the latter by secondary changes. Heat in fact gives rise to a dissociation similar to that which Arrhenius supposes to take place in dilute solutions. C. H. B.

Thermochemistry of Hydroxylamine. By BERTHELOT and ANDRÉ (*Compt. rend.*, **110**, 830—836).—Hydroxylamine nitrate was prepared by Kahlbaum in crystals which melt at about 48° and readily remain in superfusion. They are very soluble in water and very hygroscopic; heat of dissolution at 11·3 = −5·93 Cal. Decomposition by means of sodium hydroxide showed that the heat of neutralisation of hydroxylamine by nitric acid is +9·2 Cal.

The salt was mixed with naphthalene and burnt in the calorimetric bomb; the heat of combustion for 1 gram is 535·5 cal., and hence the molecular heat of combustion at constant volume is +51·41 Cal., and at constant pressure +50·29 Cal. The heat of formation in dilute solution from the constituent gases is + 23·8 Cal.

The following table gives the heats of formation of ammonia and hydroxylamine from their constituents, and the heats of formation of their dissolved salts from the acid and the gaseous constituents of the base.

Hydroxylamine ...	+23·8 Cal.	Ammonia....	+21·0 Cal.
Hydroxm. nitrate..	+33·0 „	Am. nitrate..	+33·4 „
„ chloride.	+33·0 „	„ chloride.	+33·4 „
„ sulphate.	+2×34·6 Cal.	„ sulphate.	+2×35·5 Cal.

The heats of formation of the two bases and their corresponding salts are very nearly identical. The heat of formation of hydroxylamine is slightly higher than that of ammonia, but in the case of the salts the order is reversed, ammonia having a decidedly higher heat of neutralisation than hydroxylamine. It follows that the conversion of ammonia into hydroxylamine cannot be regarded as oxidation in the proper sense of the word, nor is it a change analogous to the formation of an alcohol or an aldehyde from a hydrocarbon. The formation of hydroxylamine from nitric oxide is accompanied by the development of +45·4 Cal. The reduction of the nitro-group to hydroxylamine develops much less heat than its reduction to the amido-group, the difference being nearly equal to the heat of formation of water. Decomposition of hydroxylamine by potassium hydroxide with formation of water and ammonia develops +52·2 Cal.; decomposition by concentrated ammonia, with liberation of dissolved nitrous oxide, develops +45·0 Cal., or if the nitrous oxide escapes as gas +43·6 Cal. Simple decomposition of the hydroxylamine into nitrogen, hydrogen, and water is accompanied by the development of +45·2 Cal., and hence the energetic reducing action of the base.

The decomposition of the nitrate by heat develops +50·3 Cal. if the water is liquid and 30·9 Cal. if the water is gaseous. It follows that the decomposition, like that of ammonium nitrate, may become explosive. As with other explosives, decomposition may take place in several different ways, according to circumstances.

The oxidation of hydroxylamine to water and nitrogen or an oxide of nitrogen corresponds to the following thermal disturbances:—nitrogen +79·7 Cal., nitrous oxide +69·4 Cal., nitric oxide +58·1 Cal., nitrous anhydride +75·5 Cal., nitrogen peroxide +77·1 Cal., and nitric anhydride +95·0 Cal. The development per atom of oxygen (16 grams) in each case is +159·4, +69·4, +38·8, +37·8, +30·8, and

+31·6 respectively. Its conversion into ammonia and water by the action of hydrogen develops +66·2 Cal. C. H. B.

Preparation and Heat of Formation of Mono-sodium Erythroxide. By DE FORCRAND (*Compt. rend.*, **110**, 859—862.—The action of one equivalent of sodium hydroxide in dilute solution on a solution of erythrol at 13° develops +0·69 Cal., a number higher than the corresponding value for glycerol (+0·37), and still higher than that for glycol (+0·28), but lower than that for mannitol (+1·08). It follows that the energy of the alcoholic function increases with the number of hydroxyl-groups. 122 grams of pure dry erythrol was dissolved in 800 c.c. of methyl alcohol, which is its best solvent, the boiling solution was mixed with a solution of 23 grams of sodium in 300—350 c.c. of methyl alcohol, and the mixture boiled for five or six hours in a flask with a reflux condenser. The alcohol was afterwards distilled off in a current of dry hydrogen, and the crystals dried on porous plates out of contact with air. When heated at 115°, they lose 18·01 per cent., which corresponds with 1 molecule of methyl alcohol.

Monosodium erythroxide is obtained in this way as a very hygroscopic white powder; heat of dissolution at 13° + 0·89 Cal. From this result it follows that—

$C_4H_{10}O_4$ solid + $\frac{1}{2}Na_2O$ solid = $\frac{1}{2}H_2O$ solid + $C_4H_9NaO_4$ solid	develops	+22·815 Cal.
$C_4H_{10}O_4$ solid + NaOH solid = H_2O solid + $C_4H_9NaO_4$ solid	,,	+5·81 ,,
$C_4H_{10}O_4$ solid + Na solid = H gas + $C_4H_9NaO_4$ solid	,,	+37·70 ,,

Comparison of these numbers with the corresponding values for glycerol shows that whilst in solution the acidic function of erythrol is more energetic than that of glycerol, in the solid state the reverse seems to be the case. The anomaly is however only apparent, and is due to the fact that the physical condition of the solid erythrol is not comparable with that of the liquid glycerol. Analogy indicates that the heat of fusion of erythrol is not less than −10 Cal.

C. H. B.

Action of Erythrol on Alkali Alkyl-oxides. By DE FORCRAND (*Compt. rend.*, **110**, 904—907).—The action of sodium methoxide on erythrol (preceding abstract) yields a compound $C_4H_9O_4Na,MeOH$, which loses methyl alcohol at 140°. The action of sodium ethoxide on erythrol in presence of ethyl alcohol yields the compound $EtONa,C_4H_{10}O_4$, or if ethyl alcohol is present in large excess, the compound $EtONa,C_4H_{10}O_4,2EtOH$. Both these compounds can be heated for several hours at 150° without undergoing any alteration, and hence, in all probability, have the constitution given. This view is confirmed by thermochemical measurements. Heats of dissolution at 13°, $C_4H_9O_4Na,MeOH$ = +0·89 Cal; $EtONa,C_4H_{10}O_4$ = −1·94 Cal.; $EtONa,C_4H_{10}O_4,2EtOH$ = −5·10 Cal.

$C_4H_9O_4Na$ solid + MeOH liquid = $C_4H_9O_4Na,MeOH$ solid	develops	+0·81 Cal.
EtONa solid + $C_4H_{10}O_4$ solid = EtONa,$C_4H_{10}O_4$ solid	„	+10·80 „
EtONa,$C_4H_{10}O_4$ solid + 2EtOH liquid = EtONa,$C_4H_{10}O_4$,2EtOH solid..........	„	+8·24 „
EtONa,2EtOH solid + $C_4H_{10}O_4$ solid = EtONa,$C_4H_{10}O_4$,2EtOH solid..........	„	+10·17 „

As a rule, the heat of combination of ethyl alcohol with metallic alkyl-oxides is 1 Cal. less than for the corresponding combination of methyl alcohol, and it would follow that the combination of ethyl alcohol with sodium erythroxide would be endothermic. This result explains the non-formation of the compound $C_4H_9O_4Na$,EtOH, and also why the erythroxide is not formed in the solution in ethyl alcohol.

C. H. B.

Heats of Combustion and Formation of Nitrogenous Compounds derived from Albuminoïds. By BERTHELOT and ANDRÉ (*Compt. rend.*, **110**, 884—889).—The combustions were made in compressed oxygen in the calorimetric bomb.

	Per gram.	Molecular heat of combustion.		Heat of formation.	Diff.
		Constant volume.	Constant pressure.		
	cal.	Cal.	Cal.	Cal.	Cal.
Glycollamine	3133·6	235·0	234·9	126·2	+11·8
Alanine	4370·7	389·0	389·2	135·2	+2·8
Leucine	6526·1	854·9	855·9	158·4	−20·4
Asparagine	3396·8	448·4	448·1	205·1	+1·9
Aspartic acid	2911·1	387·2	386·8	231·9	+33·2
Tyrosine	5915·9	1070·8	1071·2	156·4	+50·0
Hippuric acid.......	5659·3	1013·0	1012·9	145·6	+60·7
Urea	—	—	—	80·8	−11·8
Uric acid	—	—	—	148·1	+37·0

The heats of formation of urea and uric acid are given for comparison. The last column gives the differences between the actual heats of combustion and those calculated from the composition by Dulong's method. In all cases except urea and leucine the actual values are higher than the calculated values, and in some instances the differences are very considerable.

In the following table, the total heat of combustion is compared with the heat of combustion of the various compounds, the nitrogen being supposed to be eliminated in the form of urea, the heat of dissolution of which approximately compensates for the heat of dissolution of the original compound and the heat of dissolution of the carbonic anhydride. These conditions closely resemble those actually existing in the living organism.

	Compounds, solid.	Compounds, dissolved.	Complete combustion.	Deficit, solid.	Deficit, dissolved.
Glycocine ..	+159·2	+167·8	234·9	75·7	78·5
Alanine	+313·5	327·5	389·2	75·7	78·5
Leucine	+780·4	811·2	855·9	75·7	78·5
Tyrosine	+995·5	942·6	1071·2	75·7	78·5
Asparagine....	266·6	274·4	418·1	151·5	156·1
Aspartic acid ..	311·1	+320·7	386·8	75·7	78·5
Hippuric acid..	937·2	+982·8	1012·9	75·7	78·5
Uric acid	158·4	+175·8	461·4	303·0	314·2

The heat developed under these conditions is very considerably lower than the heat of complete combustion, and it is evident that urea plays a very important part in connection with animal heat, since 80 to 85 per cent. of the nitrogen is eliminated in this form. If the nitrogen is eliminated in the form of uric acid, the deficit is 115·2 Cal. per 14 grams, or 122·0 Cal. if the molecule ... is in solution; if the nitrogen is eliminated as hippuric acid, the deficit is 1012·9 Cal. per 14 grams. In the case of herbivora it follows that there would be a very considerable thermal deficit, if there were not compensation in the form of liberation of free nitrogen in the intestine. The high deficit in the case of uric acid explains to some extent the effect of excessive feeding on its production, and the characteristic physiological and pathological perturbations which accompany its formation. C. H. B.

Heats of Combustion of the Chief Nitrogenous Compounds in Living Organisms, and their Relation to Animal Heat. By BERTHELOT and ANDRÉ (*Compt. rend.*, 110, 925—934).—The heats of combustion were determined by means of the calorimetric bomb. In the table (p. 938), column 1 contains the heats of combustion of 1 gram at constant pressure; column 2 the heat of combustion of the quantity which contains 1 gram of carbon; column 3 the heat of combustion if 1 gram of the nitrogen is eliminated in the form of urea, and column 4 the heat of combustion of the quantity which contains 1 gram of carbon, the nitrogen being eliminated as urea.

The table (p. 938) gives the percentage composition of the various preparations.

The albumin was purified, and dried at 100°; the fibrin was treated with ether and dried at 115°; the muscular flesh was washed with alcohol, then with ether, and dried at 115°; the hæmoglobin was prepared from the horse, and was dried at 115°; the caseïn, osseïn, and chrondrin were dried at 115°; the vitellin was dried in a vacuum at the ordinary temperature; the yolk of egg was hard-boiled and dried in a vacuum at the ordinary temperature, but was subjected to no other treatment; the vegetable fibrin was extracted with alcohol and ether and dried at 115°; the isinglass, fibroïn, and wool were washed with ether and dried at 115°; the chitin was purified; the tunicin

was prepared from Ascidians and treated with alkalis and acids, and these two substances and the gluten were dried at 115°.

	1.	2.	3.	4.
Albumin	5690	10991	4857	9381
Blood fibrin	5532	10820	4586	8970
Muscular flesh	5731	10671	4749	8841
Hæmoglobin	5915	10617	4964	8902
Casein	5629	11080	4799	9580
Osseïn	5414	10806	4544	8976
Chondrin (calf)	5346	10544	4506	8924
Vitellin	5784	11166	4954	8596
Yolk of egg	8124	12052	7704	11632
Vegetable fibrin	5836	10807	4986	9047
Crude gluten	5995	10878	5245	9338
Isinglass	5242	10800	4192	8640
Fibroïn	5097	10599	4077	8479
Wool	5567	11099	4537	9009
Chitin	4655	9943	4235	9043
Tunicin	4163	9014	4063	8794

	C.	H.	N.	O.	S.	P.	Ash.
Albumin	51·77	7·03	15·43	24·15	1·62	—	1·01
Fibrin	51·13	6·90	17·50	23·28	1·19	—	1·23
Muscle	53·71	7·38	18·19	19·54	1·18	—	2·45
Hæmoglobin	55·51	7·30	17·64	17·62	1·11	0·82	negligible
Caseïn	50·81	7·00	15·37	24·01	1·63	1·18	0·64
Osseïn	50·10	7·01	17·91	24·60	0·38	—	0·29
Chondrin	50·89	7·14	15·60	23·93	2·00	0·45	6·35
Vitellin	51·80	7·55	15·47	22·27	1·25	1·66	negligible
Yolk of egg	67·41	10·20	7·65	12·53	0·39	1·82	,,
Vegetable fibrin	53·71	7·31	17·43	20·11	1·05	0·39	,,
Crude gluten	55·11	7·53	15·73	20·30	1·00	0·33	0·21
Isinglass	48·53	6·91	18·45	25·54	0·57	—	0·74
Fibroïn	48·09	6·37	17·96	27·41	0·17	—	0·35
Wool	50·16	6·93	18·19	20·97	3·65	—	0·64
Chitin	46·82	6·76	7·77	38·50	0·15	—	—
Tunicin	45·55	6·60	1·88	45·33	0·50	0·14	—

The average heat of combustion of the albuminoïds which can serve as foods is 5691 cal. for 1 gram, and 10,870 cal. for the quantity which contains 1 gram of carbon. The loss of heat resulting from elimination of the nitrogen in the form of urea is 16 per cent. The mean heat of combustion of the carbohydrates is 9470 cal. for the quantity containing 1 gram of carbon, but the value for 1 gram varies with the degree of hydration. It is about one-fifth greater than the heat of combustion of the carbon which is present, and this reserve of energy is the source of the heat developed during many fermentations. In the case of fats, the heat of combustion per gram of carbon is 12,200 to 12,500 cal., the magnitude of this number

being due to the small percentage of oxygen which the compounds contain. On the other hand, they require a large amount of oxygen for complete combustion. In the case of the albuminoïds, about one-sixth of the total possible heat is not available, because the nitrogen is eliminated from the living organism in the form of urea; in the case of the fats and carbohydrates, the whole of the heat of combustion is available, provided that the organism is healthy and completely burns the food supplied.

When an organism is enfeebled, and is unable to burn completely the food which is introduced into it, various evil results follow. Fats are deposited in the form of adipose tissue, encumbering the muscles and other organs, and although they possess the highest heat-producing power, they are the first of the food-stuffs to cease to furnish their energy to an enfeebled organism. Incomplete combustion of carbohydrates results in a reduction of the quantity of animal heat, and appears to be connected with a pathological condition of certain special organs. Incomplete oxidation of nitrogenous compounds results in the elimination, chiefly through the kidneys, of unaltered albumin in severe cases, and of products of incomplete combustion, such as uric acid, in other cases, but the diffusion of such products in the organism is accompanied by serious perturbations.

C. H. B.

Thermochemistry of Wool and Cotton. By L. VIGNON (*Compt. rend.*, **110**, 909—910).—The heat developed by the action of normal solutions upon 100 grams of unbleached wool at 11—12° is as follows:—

	KOH.	NaOH.	HCl.	H_2SO_4.
Spun wool.........	1·16	1·15	0·95	0·99 Cal.
Combed wool	1·37	1·10	1·00	1·05 Cal.

The rise of temperature ceases after about five minutes. In the case of cotton the development of heat is slower, but the rise of temperature ceases at the end of seven or eight minutes. The heat developed per 100 grams of cotton is as follows:—

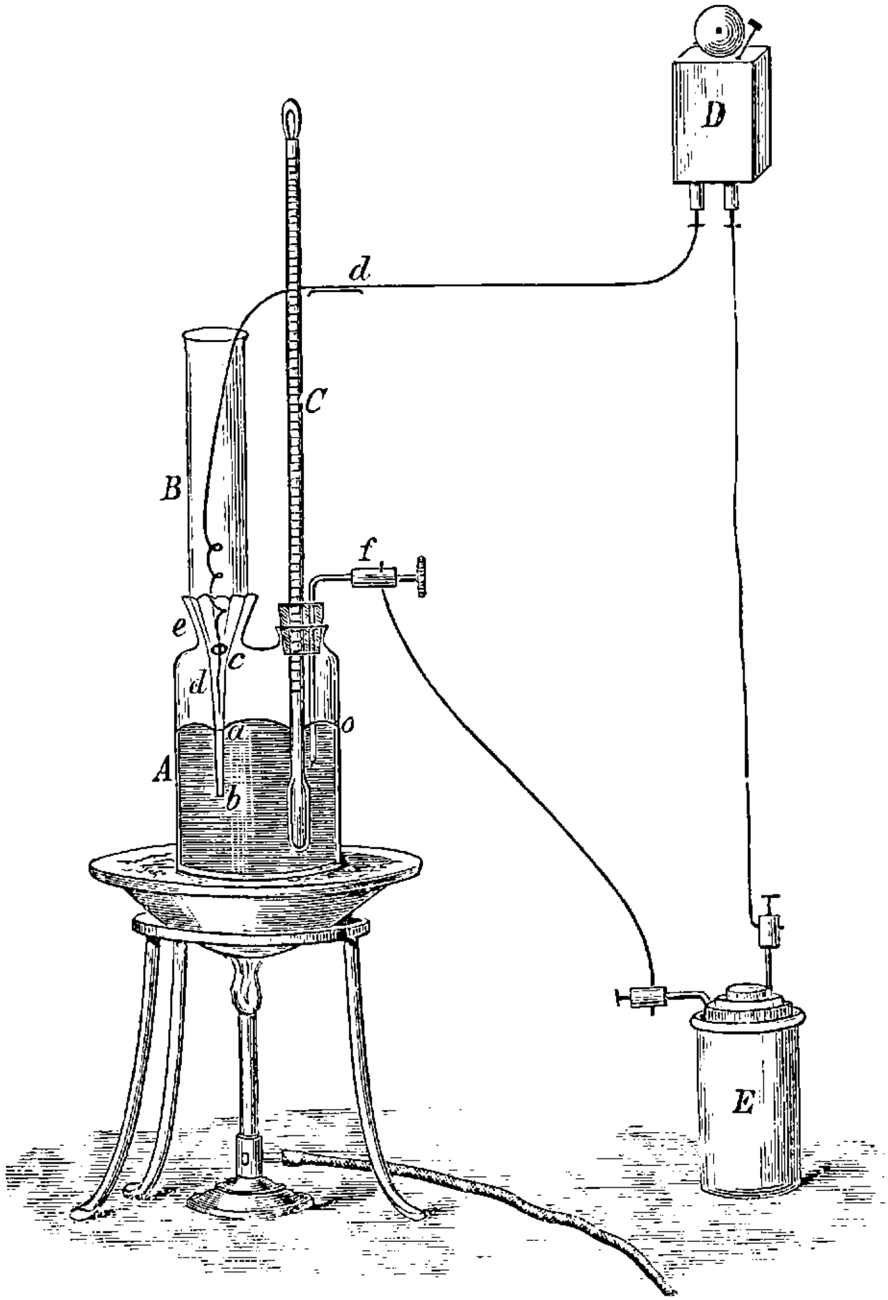
	KOH.	NaOH.	HCl.	H_2SO_4.
Cotton, unbleached .	1·30	1·05	0·65	0·60 Cal.
Cotton, bleached ...	2·27	2·20	0·65	0·58 Cal.

The greater development of heat by the action of alkalis on bleached cotton is probably due to the presence of oxycellulose, which has been formed in the process of bleaching. C. H. B.

New Apparatus for Determining Melting Points. By A. C. CHRISTOMANOS (*Ber.*, **23**, 1093—1096).—The apparatus shown in the diagram (p. 940) has been devised by the author for ensuring a more correct determination of the melting point of substances.

The cylindrical vessel (*A*), which is 12 cm. in height and 6 cm. in diameter, is heated on a sand-bath or in an air-bath, and is provided with two apertures; a thermometer (*C*) and a platinum wire (*f*) pass through a cork fitting into one of the apertures, whilst the

other (*e*) is conical and fluted, and serves for the reception of a drawn-out test-tube (*B*). The vessel (*A*) is filled with pure mercury to such a depth that the point (*b*) of the test-tube is about 2 cm. below the



surface (*ao*) of the metal. The substance is introduced, in a melted condition, into the point (*b*), so that it forms a layer of from 0·5 to 1·5 cm. in length, and when it has completely solidified again the test-tube is placed in position and the space (*ac*) immediately above the substance filled with mercury, into which dips the platinum wire (*d*). On applying heat, the mercury in (*A*) is uniformly heated throughout its whole mass, so that the thermometer and the substance are always at the same temperature; the moment the substance

melts, the two mercury columns come into contact, the circuit is completed, the bell (*D*) rings, and the temperature is noted.

F. S. K.

Boiling Points of Substances are a Function of their Chemical Nature. By M. WILDERMANN (*Ber.*, **23**, 1254—1264).—In any homologous series of organic compounds, the relation between the boiling point (in absolute temperature) under a pressure of M mm., and that under a pressure of N mm. is one and the same for all members of the series. This law has been tested in a number of cases for wide limits of pressure (12 to 1500 mm.) and found correct. It may be expressed in the following manner—

$$\frac{\mathrm{T}ap}{\mathrm{T}a\mathrm{P}} = \frac{\mathrm{T}bp}{\mathrm{T}b\mathrm{P}} = \frac{\mathrm{T}cp}{\mathrm{T}c\mathrm{P}} = \mathrm{D},$$

where *a*, *b*, and *c* represent different members of any homologous series, *p* the lower, and P the higher limit of pressure. From the above it also follows that $\mathrm{T}ap : \mathrm{T}bp = \mathrm{T}a\mathrm{P} : \mathrm{T}b\mathrm{P}$, or that the ratio of the boiling points of two substances belonging to the same homologous series is the same for all pressures.

The above law does not hold, however, for members of the same series which differ in chemical nature or in the mode of arrangement of the atoms in the molecule, and, therefore, is not applicable to the various isomerides of the higher members of a homologous series. The value of D is also found to vary from one series to another, the author having determined the values of T12 mm. / T760 mm. for 150 different substances, and found the variation to be from 0·73 to 0·79. From this it follows that the change in the boiling point of a substance with change of pressure is dependent on the nature of the elements composing that substance, as also on their number and mode of arrangement in the molecule, and hence is a function of the chemical nature of any compound.

H. C.

Solution Compounds. By G. GORE (*Chem. News*, **61**, 172—174).—The author has measured, using zinc-platinum couples, the voltaic energy of numerous aqueous solutions containing various proportions of all kinds of soluble elements, alkaline, neutral, and acid salts and acids, and has in all cases obtained evidence of combination by the reduction of voltaic energy. The author gives the average available voltaic energy of the ingredients used in the various solutions, and also the loss of voltaic energy which takes place when two of these substances are in the same solution, in proportions representing the formulæ of each solution compound.

The author considers that the results obtained illustrate the fact "that all kinds of chemical substances, when in neutral solution, unite with each other indiscriminately, and irrespective of the chemical nature of the substances."

D. A. L.

Sealing Tubes under Pressure. By A. RICHARDSON (*Chem. News*, **61**, 255).—The following device serves for sealing tubes after gases have been admitted to them under pressure. The tube

terminates in a T-piece, the lateral tube of which is constricted at places, and provided near the joint with a plug ground into a contraction of the tube, so that it acts as a valve opening inwards, yielding to the admission of gas under pressure, but closing firmly under internal pressure, and so permits of the sealing of the tube at a point further removed from the joint. D. A. L.

Inorganic Chemistry.

Spontaneously Inflammable Hydrogen Phosphide. By L. Gattermann and W. Haussknecht (*Ber.*, **23**, 1174—1190).—In order to obtain more accurate details as to the composition and properties of the liquid hydrogen phosphide obtained by Thénard in 1845, the authors have prepared this substance in considerable quantities, and subjected it to a close examination. The method of preparation adopted was that originally employed by Thénard, namely, the action of calcium phosphide on water. To obtain the calcium phosphide, a strong iron tube sufficiently wide to allow of the easy passage of a stick of phosphorus was fixed vertically in a large Hessian crucible, filled with ordinary lime, broken into pieces about the size of a hazelnut. The iron tube should end 2 cm. above the bottom of the crucible, and have a wide glass tube attached to the upper portion, in order to prevent the mouth becoming too hot. The crucible is then covered, and placed in a suitable coke furnace, heated to a moderate red heat, and phosphorus, in pieces weighing about 15 grams, thrown into the tube. The process is continued until the burning of the phosphorus from the crucible opening becomes continuous. The calcium phosphide is thus obtained as a hard, dark mass, which frequently shows iridescent surface colours, and must be at once placed in a well-closed bottle.

The decomposition of the calcium phosphide is carried out in a large, three-necked Woulffe's bottle. In the centre neck is placed a wide glass tube, dipping under the surface of the water, for the introduction of the phosphide; in the second is placed a tube, likewise dipping under the surface of the water, connected with an apparatus evolving hydrogen; whilst in the third is placed an exit tube connected with the condenser. The latter consists of a tube narrowed towards the bottom, the inlet and outlet tubes of which only come slightly below the cork, and are cut off obliquely. It is placed in a deep vessel of water containing sufficient ice at the top to keep the temperature at 0°. As soon as the air is driven out of the apparatus by the hydrogen, the Woulffe's bottle, which should contain $1\frac{1}{2}$ litres of water, is carefully heated in a water-bath until the latter has a temperature of 60°, and the calcium phosphide, broken into pieces the size of a pea, added in portions of about 2 grams. It is preferable to proceed at such a rate that 50 grams are added in

15 to 20 min. After a quarter of that amount has been added, the condensation commences, and the liquid collects in the narrow portion of the condenser. The gases which pass off still contain considerable quantities of the liquid phosphide, and if passed through a flask containing hydrochloric acid, may be converted into solid hydrogen phosphide, while the gaseous hydrogen phosphide passes off, and may be collected over water. Care must be taken in this case that the tubes do not get blocked by the deposition of the solid compound. From 1—2 c.c. of the liquid phosphide is obtained in a successful operation for every 50 grams of calcium phosphide employed.

In order to obtain a weighed quantity of the substance for analysis, a small bulb-tube with a narrow neck is blown on the condenser previous to its being used, and when the liquid has been collected, a sufficient amount passed into this bulb-tube by inclining the condenser, and the narrow neck of the former then carefully sealed. It was not found possible to estimate the phosphorus directly, but the hydrogen was readily estimated by burning the substance in a tube nearly filled with lead chromate, through which a current of dry carbonic anhydride was passed, the water formed being absorbed as usual by a calcium chloride tube. The quantity of the latter agreed well with the empirical formula PH_2.

Thénard drew his conclusions as to the composition of the liquid from the fact that it decomposed in sunlight, with formation of solid and gaseous hydrogen phosphide, the amount of the former obtained being about 38 per cent. The authors have repeated this experiment, the liquid being collected in a bulb-tube to the neck of which a small capillary tube drawn out to a point was horizontally attached. The weighed tube, after breaking off the capillary, was exposed to bright sunlight, and in 36 hours was completely converted into the solid phosphide, the amount of which was found to be 38·33 per cent. In a second experiment, the gaseous hydrogen phosphide evolved was collected over mercury and measured, the liquid being both exposed to light and heated. The quantity found was 61·28. These quantities agree well with Thénard's equation, $5PH_2 = 3PH_3 + P_2H$, and form, therefore, a further confirmation of the empirical formula PH_2.

The sealed tubes containing the liquid phosphide must not be kept for any length of time, as the decomposition commences immediately, and, after a time, the pressure becomes so great that the tubes explode with an exceptionally loud report. No deposition of the solid takes place for some time, but the liquid becomes yellow, whence it would appear that solid hydrogen phosphide is soluble in liquid phosphide.

Attempts were made to obtain the vapour-density of the liquid without success, the substance being in all cases decomposed. The comparison of the physical properties of the liquid and gaseous compounds makes the formula PH_2 improbable, and the authors, therefore, regard the formula P_2H_4 as preferable. The boiling point was found to be 57—58° under 735 mm. pressure, no residue remaining, provided the temperature of the heating bath does not rise above 80°, but the distilled compound is even more unstable than the original substance. The specific gravity of the liquid was found

in two cases to be 1·016 and 1·007, and is, therefore, slightly greater than that of water.

Unsuccessful attempts have also been made to obtain compounds of liquid hydrogen phosphide with aldehydes and ketones similar to those yielded by hydrazine. H. G. C.

Carbon Tetrafluoride. By H. MOISSAN (*Compt. rend.*, **110**, 951—954; compare Chabrié, this vol., p. 558).—Carbon fluorides are gaseous, closely resemble one another in many of their properties, and at comparatively low temperatures decompose and polymerise easily. Their preparation in a pure state is consequently difficult.

Carbon tetrafluoride can be obtained by the action of fluorine on purified carbon at the ordinary temperature; by passing fluorine into gently heated carbon tetrachloride; by passing fluorine heated to 100° into chloroform; by the action of fluorine on methane; by the action of silver fluoride on carbon tetrachloride.

Silver fluoride is heated at 195—200°, and the vapour of carbon tetrachloride is passed over it. The product is passed through a serpentine tube cooled to −23°, and is collected over mercury. The last traces of vapour of carbon tetrachloride are removed by allowing it to remain in contact with fragments of caoutchouc for some time. The gas still contains small quantities of a carbon fluoride of higher sp. gr., but can be obtained quite pure by agitating with absolute alcohol, in which the tetrafluoride is readily soluble, and from which it is expelled by heating. Alcohol vapour is finally removed by sulphuric acid. The preparation must be conducted in metal apparatus; otherwise a mixture of silicon fluoride, carbonic anhydride, carbon tetrafluoride, and a carbon fluoride of higher sp. gr. is obtained.

Carbon tetrafluoride has a sp. gr. of 3·09; it liquefies at −15° under ordinary pressure, or under 4 atmos. at 20°. It is only slightly soluble in water, and is not absorbed by sulphuric acid, aqueous potash, or aqueous baryta, but dissolves readily in ether, and especially in absolute alcohol. When heated in contact with glass, it yields carbonic anhydride and silicon tetrafluoride. When heated with sodium, it yields sodium fluoride and carbon, and it dissolves readily in alcoholic potash, which gradually converts it into potassium fluoride and carbonate. C. H. B.

Composition of Boiler Scale. By T. B. STILLMAN (*Chem. News*, **61**, 258).—An analysis of boiler scale, from a portion of the boiler exposed to direct heat, yielded the following numbers per cent.; the water of hydration being determined by igniting the scale, dried at 100°, in a tube, and collecting the water in a tared calcium-chloride tube:—

SiO_2 and clay.	Fe_2O_3; Al_2O_3.	CaO.	MgO.	CO_2.	SO_3.
11·70	2·81	11·62	41·32	6·92	0·96

Moisture.	H_2O (of hydration).	Undetermined.
0·69	21·78	0·2

The numbers show insufficient sulphuric and carbonic acids to satisfy the bases, whereas the water of hydration exactly corresponds with that required for the unsatisfied magnesium and calcium oxides, thus indicating the presence of 13·70 per cent. of calcium hydroxide and 56·37 of magnesium hydroxide. This is regarded as the result of the decomposition of the scale by heat, and was confirmed by an examination of the scale layer by layer, when it was found that the portion next to the iron, and nearest the fire, contained only traces of carbonic anhydride, but consisted principally of hydroxides; the intermediate portion was a mixture of hydroxides and carbonates; whilst the upper portion contained carbonates, but not hydroxides.

D. A. L.

Lead Phosphites and Pyrophosphite. By L. AMAT (*Compt. rend.*, **110**, 901—904).—*Normal Lead Phosphite.*—This salt is practically insoluble in water: Na_2HPO_3 diss. + $Pb(NO_3)_2$ diss. = $PbHPO_3$ pptd. + $2NaNO_3$ diss., develops + 0·65 Cal.

Lead Nitrophosphite.—If sodium hydrogen phosphite is used instead of the normal salt, part of the lead is precipitated as normal phosphite, and the liquid becomes acid. In presence of excess of lead nitrate, the normal lead phosphite combines with it, and forms a nitrophosphite, $PbHPO_3,Pb(NO_3)_2$, which can be recrystallised from dilute (1 : 10) nitric acid. The crystals are stable when exposed to air, and do not alter at 100—110°. When more strongly heated, the salt decomposes explosively, nitrogen oxides being evolved, and a white residue being left. In contact with water, the crystals are decomposed and become opaque, lead nitrate being dissolved, and the normal phosphite left. Lead nitrophosphite is also formed when lead phosphite is treated with nitric acid.

Lead hydrogen phosphite is obtained by dissolving the normal salt in a very concentrated solution of phosphorous acid, and separates on cooling in fine, transparent crystals which can be dried at 100°, and have the composition $PbH_4(PO_3)_2$. When treated with water, they become opaque, the normal phosphite being formed, whilst phosphorous acid passes into solution.

Lead pyrophosphite, $PbH_2P_2O_5$, is obtained by heating the acid phosphite at about 140° in a dry vacuum. In contact with water, it remains undissolved, but is gradually converted into the normal phosphite and phosphorous acid. The addition of lead nitrate to sodium pyrophosphite yields a precipitate of lead nitrophosphite and not of the pyrophosphite, a result due to the hydration of the pyrophosphite. The hydration takes place most rapidly in concentrated and acid solutions, and, hence, on addition of lead nitrate to the sodium pyrophosphite, precipitation of the nitrophosphite begins almost immediately, but in very dilute solutions precipitation is very slow indeed. This reaction may be utilised to distinguish between phosphites and pyrophosphites, since the former give an immediate precipitate with lead nitrate in the cold, whilst the latter, in very dilute solutions, give no precipitate until boiled. If a phosphite and pyrophosphite are mixed, the precipitate which forms in the cold is filtered off, and the filtrate is then boiled, when a further precipitate shows the presence of a pyrophosphite. C. H. B.

The Relation of the Hydrated Sesquioxides to the Salts of Iron and Aluminium. By E. A. SCHNEIDER (*Ber.*, **23**, 1349—1354).—Freshly precipitated aluminium hydroxide readily acts on a hot concentrated solution of ferric sulphate, and precipitates the whole of the iron as a basic salt. The solution of ferric sulphate, as is well known, readily dissociates into free acid and a basic salt, and in this reaction the aluminium hydroxide unites with the free acid as it is formed, and thus accelerates the precipitation. The action likewise takes place in the cold. The duration of the reaction has very little influence on the amount of alumina dissolved, but the reaction takes place more slowly in cold dilute solutious. In hot solutions the concentration is without effect on the result.

Aluminium hydroxide dissolves quickly and completely in cold solutions of normal and basic ferric chloride, alnminium chloride being formed, and colloïdal ferric hydroxide remaining in solution. The latter coagulates immediately on addition of a little sulphuric acid. A solution of ferric nitrate behaves in a similar manner.

Freshly-precipitated ferric hydroxide dissolves in a concentrated solution of aluminium sulphate in considerable quantity, forming a dark-brown solution which may be evaporated to dryness without decomposition, and yields a basic salt on addition of water, having the formula $SO_3,3Fe_2O_3,3H_2O$.

The hydroxide also dissolves in considerable quantity in aluminium chloride solution. The undissolved portion, when collected and washed, dissolves readily in large quantities of water forming a reddish-brown solution, which appears cloudy in reflected light, and shows a blue fluorescence. The solution containing the iron and aluminium loses most of its iron on addition of a trace of sulphuric acid. A solution of aluminium nitrate also takes up the ferric hydroxide, but in much smaller quantity.

Aluminium hydroxide may be partially precipitated not only from basic but also from acid solutions by means of sulphuric acid, the amount precipitated in one experiment being 25·6 per cent. Further, aluminium chloride solutions prepared from hydrochloric acid, and aluminium hydroxide which has remained for a long time under aqueous ammonia, are coagulated to a greater extent by sulphuric acid than those prepared from the freshly-precipitated hydroxide.

H. G. C.

Action of Hydrogen Peroxide on Oxygen Compounds of Manganese. By A. GORGEU (*Compt. rend.*, **110**, 857—859).—It is generally believed that when hydrogen peroxide is brought in contact with manganese peroxide, the former is rapidly decomposed into water and oxygen, whilst the latter remains unaltered. The exact nature of the change, however, depends on the conditions.

Pure crystallised manganese peroxide, obtained by heating manganous nitrate at 158—170°, decomposes hydrogen peroxide comparatively slowly, and if the latter is slightly alkaline, the manganese peroxide undergoes no change at all. If, however, the hydrogen peroxide is slightly acid, the proportion of peroxide in the manganese compound may be reduced by several per cents.

Hydrated manganese peroxide prepared in the cold immediately

decomposes hydrogen peroxide, and the former also undergoes profound alteration to an extent depending on the proportion of the hydrogen peroxide. In one case the action of 1, 2, and 3 equivalents of hydrogen peroxide containing 4 to 5 vols. of oxygen on hydrated manganese peroxide containing 97·5 per cent. of the dioxide, reduced the proportion of the latter to 75, 73, and 70 per cent.

It follows that in the estimation of hydrogen peroxide, hydrated manganese peroxide should not be used; and even with the anhydrous manganese compound, there is risk of error unless the hydrogen peroxide is slightly alkaline.

The limit at which hydrogen peroxide has no action on manganese peroxide is represented by the basic manganite $MnO_2,2MnO,\frac{1}{4}H_2O$, which can be obtained by the prolonged action of a current of air on manganous hydrate suspended in its own mother liquor. Since hydrogen peroxide reduces only the oxides above this limit, it would seem that the oxidising action of the peroxide on manganous hydroxide ought to cease at the same point. This, however, is not the case; the manganous hydroxide can be oxidised even to a higher degree than the acid manganite MnO_2,MnO. The decomposition of hydrogen peroxide is more rapid in presence of a strong base, and the oxidation of the manganese is at first partly determined by the influence of the basic function of the manganous hydroxide, assisted afterwards by the acid function of the peroxide which is formed. The higher oxidation may be regarded as due to the action of nascent oxygen. The author has previously shown that in contact with moist air the oxide $MnO_2,2MnO$ is converted into the compound MnO_2,MnO.

C. H. B.

Compounds of Ammonia with Metallic Permanganates. By T. Klobb (*Bull. Soc. Chim.* [3], **3**, 508—510; compare Abstr., 1886, 983). By the action of ammoniacal solutions of copper, zinc, cadmium, and nickel sulphates on a saturated solution of potassium permanganate at 5—10°, the compounds $Cu(MnO_4)_2,4NH_3$, $Zn(MnO_4)_2,4NH_3$, $Cd(MnO_4)_2,4NH_3$, and $Ni(MnO_4)_2,6NH_3 + 2H_2O$ are obtained. These compounds exist either as minute, dark-violet crystals or powders, are very unstable, and explode on percussion, evolving ammonia, and leaving finely-divided oxides. They dissolve in water to dark-violet solutions which decompose rapidly with separation of manganese dioxide. Their solutions in dilute sulphuric acid are unstable.

T. G. N.

Liquation of Gold and Platinum Alloys. By E. Matthey (*Proc. Roy. Soc.*, **47**, 180—186).—The author has investigated the composition of different parts of alloys containing gold and platinum, with or without admixture of copper and silver. He finds in the case of cast spheres containing respectively 88 per cent. of gold and 5 of platinum, and 70 per cent. of gold and 12 of platinum, that the platinum liquates from the gold on cooling, and becomes concentrated towards the centre of the spheres. Assays of the outer portions of such alloys are thus faulty. The same results were obtained whether

the alloy consisted entirely of gold and platinum, or whether it contained in addition silver, or copper, or both. J. W.

Iridium Dioxide. By G. GEISENHEIMER (*Compt. rend.*, **110**, 855—857).—When potassium iridate is heated to redness in a gold crucible for about an hour with 15 times its weight of a mixture of potassium chloride and bromide in equivalent proportions, it is almost completely transformed into slender, microscopic needles with a very high lustre. The product is washed first with water and then with aqua regia, and can be dried at 100° or even 150° without decomposition. It consists of pure iridium dioxide, and when heated in hydrogen yields metallic iridium free from any trace of alkali.

The dioxide can also be obtained in an amorphous condition by heating iridium to bright redness in contact with the air or with oxygen. Whether crystallised or amorphous, iridium dioxide which has been prepared at a high temperature is not attacked by ordinary solvents.

Hydrated iridium dioxide is obtained (1) by boiling a 30 per cent. solution of potassium iridate with a large excess of ammonium chloride; (2) by boiling the blue basic iridate obtained in the preparation of potassium iridate with excess of ammonium chloride, a method which has the disadvantage that any silica, iron, or ruthenium present is precipitated at the same time; (3) by heating three parts of iridium to redness for 2 or 3 hours in a gold crucible with 10 parts of sodium hydroxide and 3 parts of sodium nitrate. The product seems to be sodium iridate, but is very unstable, and when boiled with water rapidly decomposes, oxygen being evolved and iridium dioxide precipitated. The dioxide is rapidly washed with ammonium chloride solution and dried at 100°; it is dissolved even by dilute acetic acid. A similar result is obtained with barium hydroxide and barium nitrate, but the separation of barium carbonate during subsequent operations is very inconvenient. C. H. B.

Mineralogical Chemistry.

Eukairite from Argentine. By R. OTTO (*Ber.*, **23**, 1039—1041).—The author has analysed a mineral obtained from Rioja, in the Argentine Republic, and finds it to be identical with eukairite, which occurs in small quantities in Småland, Sweden. The analysis showed that the mineral contains an equal number of atoms of silver, copper, and selenium, and agreed to a certain extent with Berzelius' analysis of the Swedish mineral. F. S. K.

Chemical Constitution of Talc. By F. W. CLARKE and E. A. SCHNEIDER (*Ber.*, **23**, 1537—1540).—Talc has usually been regarded as a magnesium hydrogen metasilicate, $H_2Mg_3(SiO_3)_4$, but lately Groth

has proposed to regard it as a basic pyrosilicate, $Mg(Si_2O_5)_2(MgOH)_2$. The authors think Groth's formula incorrect because talc is scarcely attacked by hydrochloric acid; when heated for 15 hours at 400° in a current of hydrogen chloride, only 0·23 per cent. of magnesia is converted into chloride, and when digested with aqueous hydrochloric acid of sp. gr. 1·14 for 32 days, only 4 per cent. is converted. But minerals which contain the group —Mg·OH are easily decomposed by hydrochloric acid.

Further, if Groth's formula is correct, the molecule of talc should not be decomposed when heated, but should simply lose a molecule of water between the two (MgOH) groups. According to the usual formula, the following decomposition should take place:—

$$H_2Mg_3(SiO_3)_4 = H_2O + SiO_2 + 3MgSiO_3;$$

and, as a matter of fact, it is found that, after talc has been heated for half an hour over the blowpipe, it loses one fourth of its silica when boiled with aqueous soda, although before ignition it is unattacked by this agent. C. F. B.

Organic Chemistry.

Vapour-density and Melting Point of Cyanogen Iodide. By K. Seubert and W. Pollard (*Ber.*, **23**, 1062—1065).—Vapour-density determinations of cyanogen iodide in V. Meyer's apparatus at 183° and 250° gave results which agree well with those required by molecular formula CNI; the compound undergoes slight dissociation, and iodine is deposited on the cooler portions of the tube. Cyanogen iodide melts at 146·5°, and solidifies again at 142·5°. F. S. K.

Thiocyano- and Selenocyano-derivatives. By L. Hagelberg (*Ber.*, **23**, 1083—1092).—*Trimethylene thiocyanate*, $CH_2(CH_2{\cdot}S{\cdot}CN)_2$, is formed when trimethylene bromide is boiled with potassium thiocyanate in alcoholic solution. It crystallises in colourless plates, melts at 23°, and is soluble in alcohol, ether, and hot water. The *sulphide*, $C_3H_6S_2$, is obtained when the thiocyanate is treated with 25 per cent. alcoholic potash; it is a colourless, crystalline powder, melts at 71°, and is insoluble in water, alcohol, and ether, but soluble in benzene, cumene, nitrobenzene, warm potash, nitric acid, and sulphuric acid. The constitution of this compound is probably expressed by the formula $C_3H_6<{S_2 \atop S_2}>C_3H_6$, as when ethylene thiocyanate is treated with alcoholic potash, it is converted into diethylene tetrasulphide, $C_2H_4<{S_2 \atop S_2}>C_2H_4$.

Trimethylene mercaptan, $CH_2(CH_2{\cdot}SH)_2$, prepared by reducing the thiocyanate with zinc and hydrochloric acid, or by treating trimethylene bromide with potassium hydrosulphide in alcoholic solu-

tion, is a colourless, disagreeably smelling oil boiling at 169°. In its alcoholic solution, lead salts produce a yellow, copper sulphate a green, and mercuric chloride a colourless precipitate; it combines with yellow mercuric oxide very energetically, yielding a grey mass, and on oxidation it is converted into the sulphide described above.

Propylene thiocyanate, $CN{\cdot}S{\cdot}CHMe{\cdot}CH_2{\cdot}S{\cdot}CN$, is a brown oil which is insoluble in water and cannot be distilled; when treated with alcoholic potash, it is probably converted into the sulphide, which cannot, however, be isolated.

Propylene mercaptan, $SH{\cdot}CHMe{\cdot}CH_2{\cdot}SH$, is a colourless, disagreeably smelling oil boiling at 152°. It readily oxidises when heated in the air, being converted into the sulphide, and it combines very energetically with mercuric oxide; in its alcoholic solution, lead nitrate produces a yellow, and mercuric chloride a colourless precipitate.

An oil, probably *isobutylene mercaptan*, is formed in very small quantities, with evolution of butylene and hydrogen sulphide, when isobutylene bromide is treated with potassium hydrosulphide in dilute alcoholic solution; this mercaptan is also produced, but only in small quantities, when isobutylenedisulphonic chloride is reduced with zinc and sulphuric acid.

Trimethylene selenocyanate, $CH_2(CH_2{\cdot}Se{\cdot}CN)_2$, prepared by boiling trimethylene bromide with potassium selenocyanate in alcoholic solution, is a colourless, hygroscopic, crystalline compound melting at 51°; it has a disagreeable odour, is soluble in alcohol, ether, and glacial acetic acid, and is readily oxidised by warm nitric acid. The *selenide*, $(C_3H_6Se_2)_n$, obtained by treating the selenocyanide with alcoholic potash, melts at 54·5°, and is insoluble in ether, but soluble in benzene, glacial acetic acid, and hot alcohol.

Propylene selenocyanate, $CN{\cdot}Se{\cdot}CHMe{\cdot}CH_2{\cdot}Se{\cdot}CN$, is a colourless, crystalline, disagreeably smelling compound melting at 66°; it is soluble in ether, glacial acetic acid, benzene, and acetone, and decomposes on exposure to light with separation of selenium.

When isobutylene bromide is treated with potassium selenocyanate in alcoholic solution, the compound $C_3N_3Se_4K + H_2O$, described by Verneuil (Abstr., 1884, 1109), is produced.

Ethylene selenide, $(C_2H_4Se_2)_n$, is obtained when ethylene selenocyanate (m. p. 138°) is treated with alcoholic potash; it separates from ethylene bromide in crystals, melts at 130·5°, and is insoluble in alcohol and ether, and only sparingly soluble in benzene and glacial acetic acid. F. S. K.

Preparation of Sodium Erythyroxide; Action of Erythrol on Alkali Alkyl-oxides. By DE FORCRAND (*Compt. rend.*, **110**, 859—862, and 904—907).—See this vol., p. 935.

Alcoholic Fermentation of Invert Sugar. By U. GAYON and E. DUBOURG (*Compt. rend.*, **110**, 865—868).—When invert sugar is fermented with ordinary yeasts, the lævorotatory power gradually increases, attains a maximum, and then decreases, finally becoming nil. This series of changes is due to the fact that the dextrose ferments more rapidly than the levulose. Most of the pure species of

commercial yeasts behave in the same way, and the relation between the rotatory power and the total quantity of sugar fermented is represented by a parabolic curve, the form of which is constant for the same yeast under the same conditions, but varies considerably with different species. In some cases, the two sugars ferment at nearly the same rate, whilst with other species the dextrose ferments much more rapidly than the levulose. The curves are therefore more or less flattened, but their curvature is always in the same direction, and the liquid is always lævogyrate. They are but slightly modified by temperature, concentration, acidity, and other conditions. There are, however, four species of yeast which ferment levulose more rapidly than glucose. One of the most active of these is *Saccharomyces exiguus*, an inversive yeast. The rotatory power of the liquid rapidly diminishes, changes in sign, reaches a maximum, and then again decreases, finally becoming nil. The curves in the four cases are parabolic, but their curvature is in the opposite direction to that of the curves in the previous cases; they are also affected to a much greater extent by differences of temperature and the constitution of the fermented liquid. C. H. B.

Indian Geranium Oil. By F. W. SEMMLER (*Ber.*, **23**, 1098—1103; compare Dodge, this vol., p. 231).—Indian geranium oil, derived from *Andropogon schœnanthus*, L., has sp. gr. = 0·8869 at 16°, and a column 100 mm. long rotates the plane of polarised light 20′ to the left. It was fractionated under a pressure of 17 mm., and the fraction boiling at 120·5—122·5°, which amounted to 92 per cent. of the whole, was examined. It has the constitution $C_{10}H_{18}O$, and an index of refraction = 1·4745 at 20°, giving a refraction-equivalent of 48·71; hence, applying Brühl's method, it contains 2 ethylene unions. This is confirmed by the fact that 1 mol. unites with 4 atoms of iodine. Now a substance of the formula $C_{10}H_{18}O$ containing 2 ethylene unions cannot be a ring compound; it is therefore a doubly unsaturated alcohol, its alcoholic properties being otherwise known. When oxidised, 1 mol. yields 1 mol. of isovaleric acid. When cautiously treated with phosphoric anhydride and distilled at 17 mm., it yields a mixture of hydrocarbons, including a terpene boiling at 60—65°, and a polyterpene boiling at 205—215°; these have not yet been fully investigated, but they are certainly ring compounds. Indian geranium oil can therefore have either of the two formulæ:— $CHMe_2·CH_2·CH⁚CH·CHMe·CH⁚CH·OH$ if optically active, and $CHMe_2·CH_2·CH⁚CH·CMe⁚CH·CH_2·OH$ if optically inactive. Probably the latter is correct, as the ether, $(C_{10}H_{17})_2O$, readily yields a sulphide, $(C_{10}H_{17})_2S$. C. F. B.

Stereochemistry of Nitrogen-compounds. By C. WILLGERODT (*J. pr. Chem.* [2], **41**, 526—528).—The author has already published a paper touching on this subject (*J. pr. Chem.* [2], **37**, 449; Abstr., 1888, 949). The theories of Behrend (this vol., p. 575) as to the constitution of ammonia and its derivatives are very similar to those expressed in the said paper, which, however, Behrend has failed to notice. The existence of positive and negative poles in nitrogen-

compounds cannot be supported by analogy with compounds of elements of the same group as nitrogen. A. G. B.

Chloramylamines. By A. Berg (*Compt. rend.*, **110**, 862—865). —*Chloramylamine* is obtained by treating a neutral solution of amylamine hydrochloride with a neutral solution of sodium hypochlorite containing a molecule of active chlorine for each molecule of the amine. The product is washed with water and dried over anhydrous sodium sulphate. It is an oily, almost colourless liquid, with a faint, pungent odour; sp. gr. at 0° = 0·968. It gradually solidifies and yields dichloramylamine, amylamine hydrochloride, and a liquid which is also obtained by the action of amylamine on dichloramylamine, and which has not yet been investigated. The same decomposition takes place with violent ebullition if a small quantity of the liquid is heated in a tube. Acids convert the chloramylamine into amylamine and dichloramylamine.

Dichloramylamine can also be obtained by the action of sodium hypochlorite (containing 2 mols. of active chlorine) on amylamine hydrochloride mixed with 1 mol. of hydrochloric acid. It is obtained most easily by the process used by Tcherniac for the preparation of dichlorethylamine. It is washed with dilute sodium thiosulphate solution, dilute sulphuric acid, and water, and dried over anhydrous sodium sulphate. It is a golden-yellow, oily liquid with a very irritating odour, and is stable when pure; sp. gr. at 0° = 1·063. It boils at 49° under a pressure of 14 mm., and at 58° under 22 mm. Under atmospheric pressure it boils at about 142°, but the greater part decomposes, and the decomposition may become explosive. A mixture of dichloramylamine (1 mol.) and amylamine (2 mols.) develops heat, and partially solidifies, with formation of amylamine hydrochloride, and a liquid which is under investigation.

Chlorodiamylamine is obtained by treating a warm solution of diamylamine hydrochloride with sodium hypochlorite, active chlorine and the amine being present in equal molecular proportions. It is a colourless, oily liquid with a feeble odour; sp. gr. at 0° = 0·897. It solidifies to a white mass at −20°, and at the ordinary temperature slowly decomposes and deposits white leaflets. When heated under atmospheric pressure, it decomposes with violent decrepitation, but under a pressure of 12 mm. it boils at about 89°. When mixed with amylamine, there is no reaction in the cold, but the mixture solidifies if heated. C. H. B.

Action of Ammonia on Di- and Tri-halogen Substitution-products of Hydrocarbons. By P. Galewsky (*Ber.*, **23**, 1066—1069).—When ethylene bromide (30 grams) is dissolved in a saturated alcoholic solution of ammonia (10 parts), and the mixture kept for 10 days at the ordinary temperature, and then evaporated on the water-bath, a residue is obtained which contains ethylenediamine; if this residue is dissolved in water, and treated with benzoic chloride, several grams of dibenzoylethylenediamine are obtained.

Propylene bromide is not acted on by alcoholic ammonia at the

ordinary temperature, but at 100° the formation of the diamine takes place.

When allyl tribromide is treated with alcoholic ammonia at the ordinary temperature, or at 100°, it is converted into a bromallylamine, identical with the compound described by Paal and Hermann (Abstr., 1889, 116). The *benzoyl*-derivative, $C_3H_4Br\cdot NHBz$, crystallises from hot water in plates, and from light petroleum in needles, melts at 97—98°, and is insoluble in cold water, but soluble in hot benzene, ether, chloroform, and glacial acetic acid. F. S. K.

Constitution of the Cobalt-bases. By S. M. JÖRGENSEN (*J. pr. Chem.* [2], **41**, 429—439).—The author discusses this question in the light of his experiments on the ethylenediaminepraseocobalt salts (see next abstract); the paper does not admit of useful abstraction.

A. G. B.

Metallic Diamine-compounds. By S. M. JÖRGENSEN (*J. pr. Chem.* [2], **41**, 440—459; compare Abstr., 1889, 351).—*Ethylenediaminedichloropraseocobalt platinosochloride*, $2CoCl_3,4C_2H_4(NH_2)_2,PtCl_2$, is precipitated when the chloride is mixed with potassium platinosochloride; it forms dark-green, microscopic tables. The *bromide*, $CoCl_2Br,2C_2H_4(NH_2)_2$, is obtained when a solution of the chloride (2·7 grams) in water (10 c.c.) is mixed with strong hydrobromic acid (10 c.c.), and the resulting *hydrobromide* dried over potassium hydroxide; it is a green powder. The *dithionate* was also obtained.

Ethylenediaminedibromopraseocobalt bromide is best obtained by triturating the dichloro-chloride (5 grams) with freshly prepared silver oxide (12 grams) and water, filtering, adding strong hydrobromic acid (10—12 c.c.) to the filtrate, and evaporating to dryness; it is green, and is less soluble in water than the dichloro-chloride. Its reactions with various reagents are described. The *hydrobromide*, $CoBr_3,2C_2H_4(NH_2),HBr + 2H_2O$, the *nitrate*, $NO_3\cdot CoBr_2,2C_2H_4(NH_2)_2$, the *platinochloride* (with 3 mols. H_2O), the *platinobromide*, the *mercurobromide*, and the *dithionate* are described.

A series of violeocobalt salts, isomeric with the praseo-salts, have been obtained from the latter.

Ethylenediaminedichlorovioleocobalt chloride, $CoCl_3,2C_2H_4(NH_2)_2$, is obtained by evaporating a solution of the praseochloride (5 grams) in water (50 c.c.) to dryness, and drying the residue at 102—103° until it is constant in weight. As the conversion is not quite complete, the residue is washed with a little cold water until the washings appear of a deep-violet, and then with alcohol. The air-dried salt contains 1 mol. H_2O, and is a coarse, violet powder; it is less soluble than the praseo-salt, requiring 25 parts of cold water. It is insoluble in alcohol, but is precipitated with difficulty by that liquid from its aqueous solution; ether, however, precipitates it in flat, dichroic needles. Its aqueous solution becomes red after a time, from the formation of the roseo-salt, which is converted into the praseo-salt by sodium hydroxide or silver oxide; evaporation with hydrochloric acid also converts it into the praseo-salt. Its reactions with various reagents are given. The *platinochloride*, the *platinosochloride*, the *mercurochloride*, the *nitrate*, and the *dithionate* are described.

Amine-ethylenediaminechloropurpureocobalt chloride,

$$CoCl_3,2C_2H_4(NH_2)_2,NH_3 + 2H_2O,$$

is obtained when dilute ammonia is added to an aqueous solution of the dichloropraseo-chloride, and the whole evaporated to dryness; the residue is dissolved in water and concentrated over sulphuric acid, when the salt crystallises in large, dark-red needles. Its reactions are given, and the corresponding *platinochloride*, *platinosochloride*, *nitrate*, and *dithionate* are described. When the dichloroviolco-chloride is similarly treated with ammonia, the same compound is obtained.

A. G. B.

Dimethylethylenediamine. By A. ANGELI (*Ber.*, **23**, 1357—1359).—Diacetyldioxime, on reduction with sodium in alcoholic solution according to Ladenburg's method, is readily converted into *dimethylethylenediamine*, which may be isolated by distilling the product of the reaction in a current of steam. It forms a crystalline, very hygroscopic hydrochloride, whilst the *aurochloride*,

$$(C_4H_{12}N)_2,2HAuCl_4,$$

forms orange-yellow crystals, moderately soluble in water and melting at 238°. The *oxalate*, $C_4H_{12}N_2,C_2H_2O_4$, forms small, white crystals, which are soluble in water but are reprecipitated from the solution by alcohol; it becomes yellow at 235°, and melts at 237·5—238°.

H. G. C.

Formaldehyde. By W. ESCHWEILER (*Chem. Centr.*, 1890, i, 582—583, from *Inaug. Diss. Univ. Rostock*).—The author has employed the method of Tollens and Loew for the preparation of formaldehyde. He finds that the best yield is obtained if the copper spirals are kept at such a low red heat that they can only be seen to glow in the dark. In the first receiver a product may then be obtained containing 40 per cent. of the aldehyde; the mixed products from all the receivers contained from 17 to 18 per cent. of the aldehyde.

The unpurified aldehyde solution contains formic acid, and after neutralising this with calcium hydroxide, it still becomes acid on exposure to the air.

The determination of the formaldehyde was made according to Legler's method (Abstr., 1889, 1250), also by oxidation with chromic acid. By distilling with a long (30 cm.) dephlegmator, a solution containing 20·99 per cent. by weight of formaldehyde was obtained. This boiled at 97·5—99° and had a sp. gr. of 1·063. Experiments made with the object of obtaining a more concentrated solution of the aldehyde by fractional distillation from 50° upwards, resulted in the formation of oxymethylene. On the other hand, oxymethylene decomposes again by protracted contact with water, and the nature of the resulting product, either formaldehyde or oxymethylene, is therefore under the will of the operator. The author finds that in dilute solutions the formaldehyde is almost pure. He was not able to prepare diformaldehyde or the α-trihydroxymethylene described by Pratesi. In the more concentrated solutions of formaldehyde, methyleneglycol appears to be present.

The author has prepared the sodium hydrogen sulphite compound, $NaHSO_3,CH_2O + H_2O$, crystallising in plates which disintegrate when exposed to the air; the corresponding potassium compound, $KHSO_3,CH_2O$, forms plate-like crystals.

Methylenedipiperidine, $CH_2(C_5NH_{10})_2$, a colourless oil with alkaline reaction, is prepared by the action of formaldehyde sodium hydrogen sulphite on piperidine in aqueous solution. It is but little soluble in water, readily soluble in alcohol, ether, chloroform, &c. Its sp. gr. = 0·9132 at 24°. It does not form salts. J. W. L.

Parapropaldehyde and Metapropaldehyde. By W. R. ORNDORFF (*Amer. Chem. J.*, **12**, 352—354).—When ordinary propaldehyde, boiling at 49°, is cooled in a freezing mixture and treated with a few bubbles of hydrogen chloride, *parapropaldehyde* and a small quantity of *metapropaldehyde* are simultaneously formed. After remaining in a freezing mixture, the metapropaldehyde may be collected. It is a light, crystalline solid resembling ordinary metaldehyde very closely; is insoluble in water, but dissolves in ether, chloroform, and benzene, more sparingly in alcohol and acetic acid. It melts at 180°, and, at temperatures slightly above, sublimes readily, forming fibrous, rounded needles, which show no crystal faces. Attempts to obtain derivatives were without success. Parapropaldehyde is present in the filtrate from the metapropaldehyde, and may be obtained from it by distillation under a reduced pressure of 50 mm., when it boils at 85—86°. It is a colourless liquid, lighter than water; has the odour of ordinary paraldehyde, and if cooled to −20°, forms a mass of crystals resembling those formed on cooling paraldehyde to 0°. It is not very soluble in water, and this property may be taken advantage of to separate it from propaldehyde, which is freely soluble. Both meta- and para-propaldehydes are converted into ordinary propaldehyde on heating with sulphuric or hydrochloric acids, a small amount of a tarry product being at the same time formed. G. T. M.

α-Dichloropropaldehyde. By W. SPRING and E. TART (*Bull. Soc. Chim.* [3], **3**, 402—405).—On fractionating the product of the action of dry chlorine on propyl alcohol, in addition to propyl chloride boiling at 47—50°, an oily liquid distilling at 120—150° is obtained, from which, after a time, small, colourless needles separate. These melt at 111—112°, and do not recrystallise on cooling, are insoluble in water, but very soluble in light petroleum, chloroform, ether, and alcohol, and are purified by recrystallisation from the latter solvent; at 100°, they sublime in long, nacreous needles.

When heated with moist silver oxide at 150—170° in sealed tubes, silver is deposited as a mirror, and silver chloride, carbonate, and acetate are formed; the original substance on reduction with zinc and acetic acid yields normal propyl alcohol. The crystalline substance is therefore a polymeride of αα-dichloropropaldehyde, $CH_3{\cdot}CCl_2{\cdot}COH$, which is isomeric with the αβ-derivative, $CH_2Cl{\cdot}CHCl{\cdot}COH$, obtained, by Aronstein, from acroleïn.

The liquid from which these crystals separated contains the compound $CH_3 \cdot CH_2CCl_3$, together with other chloro-derivatives.

T. G. N.

Action of Sodium on Acetone. By P. C. FREER (*Amer. Chem. J.*, **12**, 355—357).—If acetone is treated with metallic sodium, a reaction takes place resembling that of sodium on methyl and ethyl alcohols, free hydrogen is evolved, and a white, flaky solid, sodium acetonate, is produced. The best results are obtained if the metallic sodium is finely powdered and covered with a large amount of anhydrous ether, the acetone mixed with four or five times its own volume of the same medium, and then slowly added to the sodium by means of a dropping-funnel, the whole operation being conducted in a stream of pure and dry hydrogen. By this means, the reaction is rendered less violent, only slight reduction of the acetone to isopropyl alcohol takes place, and the sodium acetonate separates in white flakes and may be freed from ether by placing it over solid paraffin, in a vacuum. The compound rapidly changes in presence of air, which explains the excess of sodium experimentally found over that calculated for C_3H_5NaO. On addition to hydrochloric acid, acetone is regenerated, and on exposure to air before addition to hydrochloric acid, an oil is formed which in all probability corresponds with that obtained by Fittig (*Annalen*, **110**, 25), who did not study the properties of the sodium compound, but contented himself with the preparation of pinacone. Attempts to prove the constitution of sodium acetonate by converting it into ethyl acetoacetate by the addition of ethyl chlorocarbonate were without success, an oily compound boiling at 185—200° being the chief product.

G. T. M.

Products formed in the Distillation of Wood. By VLADESCO (*Bull. Soc. Chim.* [3], **3**, 510—514).—The author has examined two fractions obtained from the rectification of methyl alcohol. From one, passing over at 85—140°, he separated methyl propyl ketone, boiling at 101—103°, whilst the other sample, which distilled at 70—143°, consisted to the extent of 75 per cent. of methyl ethyl ketone boiling at 79—82°, which was also contained to a smaller extent in the former fraction. Acetone, toluene, and xylene also occurred. He suggests the material as a source for these compounds.

T. G. N.

Action of Ethyl Iodide on Amido-acids. By E. DUVILLIER (*Bull. Soc. Chim.* [3], **3**, 503—507).—When ethyl iodide is heated in a reflux apparatus with solutions of amido-α-butyric acid or of amidopropionic acid in alcoholic potash, care being taken to keep the mixture alkaline throughout the operation, there is formed in the former case diethamido-α-butyric acid, and in the latter case diethamido-α-propionic acid, which are characterised by their copper salts (compare Abstr., 1885, 750, and 1889, 1139). The yield is almost theoretical, and no betaïne is produced.

T. G. N.

Action of Trimethylamine on Ethyl Bromisovalerate. By E. DUVILLIER (*Bull. Soc. Chim.* [3], **23**, 507—508).—Trimethylamine (2 mols.), and ethyl bromisovalerate (1 mol.) are heated in sealed tubes at 90° for some hours. On cooling, much trimethylamine

bromide separates. The mother liquor is treated with hot baryta-water to remove trimethylamine, neutralised by sulphuric acid, and distilled. After removal of bromine from the residue by silver oxide, platinic chloride is added, and tetramethylammonium platinochloride is precipitated, and, by subsequent careful crystallisation of the mother liquor, a small quantity of minute, transparent, orange prisms of a betaïne platinochloride separate, which contain 26·64 per cent. Pt, and correspond with the formula $COOH\cdot CHPr^{\beta}\cdot NMe_3Cl,PtCl_4 + 4H_2O$, being derived from some trimethylamidoisovaleric acid or methylisovalerylbetaïne produced in the reaction. The distillate above mentioned contains dimethylacrylic acid amounting to 25 per cent. of the bromo-derivative employed and some isovaleric acid.

T. G. N.

Ethoxyacrylic Acid from α-Dichloropropionic Acid. By R. OTTO (*Ber.*, **23**, 1108—1110).—Merz has lately obtained this substance, $CH_2{:}C(OEt)\cdot COOH$, by treating α-dibromopropionic acid melting at 60—61° with alcoholic potash. Holst has prepared the same substance by treating with alcoholic potash the α-dichloropropionic acid boiling at 185—190°, which was obtained from the corresponding α-dichloropropionitrile, and first thoroughly investigated by the author. α-Dichloropropionic acid (1 mol.) was heated for three hours with alcoholic potash (4 mols.) in a sealed tube on the water-bath. Merz's method was then followed; the solution was freed from potassium chloride, the alcohol evaporated, and the residue extracted with ether. When evaporated, the ethereal solution left an oily residue; this was repeatedly treated with light petroleum, and the solution thus obtained concentrated, when a small quantity of white crystals of ethoxyacrylic acid was obtained, melting at 110° after recrystallisation from hot benzene. The author remarks in conclusion that in a paper published in conjunction with Beckurts (Abstr., 1885, 509), and apparently everlooked by Merz, he had already anticipated a portion of the latter's work.

C. F. B.

α-Dichloro-substitution Products of Dimethylsuccinic Acid. By R. OTTO and G. HOLST (*J. pr. Chem.* [2], **41**, 460—483).—The authors have investigated the conditions most favourable for the production of α-dichloro-symmetrical-dimethylsuccinic (dichloradipic) and pyrocinchonic acids by the action of silver on dichloropropionic acid (Otto and Beckurts, Abstr., 1878, 290; 1885, 753). They find (1) that the more finely divided the silver, the more rapid is the process and therefore the purer the product; (2) that heating under pressure at a higher temperature accelerates the process, but increases the secondary products; (3) that the dichlorodimethylsuccinic acid is somewhat freely soluble in the oily secondary products and is thereby decomposed. The acids are best separated by dissolving them from the reaction-mass with ether, evaporating, picking out the crystals of α-dichloro-symmetrical-dimethylsuccinic acid from the yellow oily residue, and then adding water to precipitate the pyrocinchonic acid.

α-Dichloro-symmetrical-dimethylsuccinic anhydride, obtained by the action of acetic chloride or phosphoric chloride on the acid, forms

small crystals of the consistency of camphor; it dissolves in the usual solvents and is converted into the acid by water. No geometrical isomeride of this dichlorodimethylsuccinic acid was obtained by heating the acid with its anhydride (compare the action of reducing agents, Abstr., 1885, 755). When the anhydride is treated with alcoholic ammonia, it is converted into *ammonium α-dichloro-symmetrical-dimethylsuccinamate;* this partially crystallises from hot alcohol in white, silky spangles. The free *acid* forms a white, crystalline powder. When the ammonium salt is heated in 50 per cent. alcohol for some time, carbonic anhydride is evolved, and ammonium chloride and *chlorotiglamide* separate; the latter forms prismatic crystals which melt at 108°.

When an aqueous solution of sodium α-dichloro-symmetrical-dimethylsuccinate is heated in a reflux apparatus, two α-methyl-β-chlorocrotonic acids, $C_5H_7ClO_2$ (chlorotiglic acid; Otto and Beckurts, *loc. cit.*), are formed together with methyl ethyl ketone. The mixture of the two acids melts at 55—68°, and by fractional crystallisation can be separated into lustrous, white, large, flat needles melting at 55—63°, and large, clear, rhombic prisms melting at 63—73°. By slowly subliming the crystals of lower melting point, needles are obtained which melt at 55°.

The acid of higher melting point is obtained, together with methyl ethyl ketone when α-dichloro-symmetrical-dimethylsuccinic acid is heated with water at 120°; it melts at 73°, and is more soluble in water than the acid melting at 55°; its crystallography is given. This acid is identical with the α-methyl-β-chlorocrotonic acid obtained by Rucker from methyl ethyl acetoacetate and phosphoric chloride.

These two acids are geometrical isomerides and may be formulated thus: $\begin{matrix}\text{Me·C·Cl}\\ \Vert\\ \text{Me·C·COOH}\end{matrix}$ (m.p. 73°), and $\begin{matrix}\text{Cl·C·Me}\\ \Vert\\ \text{Me·C·COOH}\end{matrix}$ (m.p. 55°).

When α-methyl-β-chlorocrotonic acid is heated with fuming hydrochloric acid at 140—150°, carbonic anhydride is separated, and a dichlorobutane is formed. A. G. B.

The so-called Dihydroxymaleic Acid. By W. S. HENDRIXSON (*Amer. Chem. J.*, **12**, 325—329).—The announcement of the discovery of this acid was made by Bourgoin (this Journal, 1873, 1021; 1875, 356), who claimed to have prepared it by the action of water on the silver salt of dibromomaleic acid. As some doubt has been thrown on the existence of the acid by Scherks (*Annalen*, **207**, 223), the author has thought it desirable to repeat Bourgoin's work. The dibromomaleic acid needed was obtained by the oxidation of mucobromic acid with cold fuming nitric acid, and the pure silver salt prepared. This was heated with water in sealed tubes at 150°, according to the method employed by Bourgoin. On opening the tubes, which contained a considerable quantity of silver bromide, much carbonic anhydride escaped. The strongly acid contents of the tube were steam-distilled, when the whole of the acid readily volatilised, and was found to consist entirely of acetic acid. The author supposes that, in this reaction, the formation of acetic acid is preceded by that

of the ketonic acid, COOH·CO·CH(OH)·COOH, which would readily give rise to acetic acid and 2 molecules of carbonic anhydride.

G. T. M.

Acetone-chloroform; Chlorisobutyric Trichloride; Ethyl Acetone-chloroform. By C. WILLGERODT and S. SCHIFF (*J. pr. Chem.* [2], **41**, 515—526).—*Chlorohydroxyoxydipropionic acid*,

COOH·CMe(OH)·O·CMeCl·COOH,

is the product of the action of sulphuric acid (100 grams) on acetone-chloroform (10 grams), and is extracted by ether from the reaction-mass; it forms large, white, feathery crystals melting at 31·5° and boiling at 183°. It is very deliquescent and soluble in all solvents. It appears to be a bibasic acid. The *barium*, *lead*, and *copper* salts (each with 2 mols. H_2O), and *cobalt* and *nickel* salts were obtained.

Oxydiethylidenelactic acid, O[CMe(OH)·COOH]$_2$, is obtained as its *primary potassium salt* when the above acid is neutralised with potash; the liquid becomes slightly warm and potassium chloride separates out. If the liquid is hot to begin with, the *secondary potassium salt* is formed. The free acid does not crystallise.

The action of phosphoric acid, hydrochloric acid, nitric acid, and ammonia respectively on acetone-chloroform is described, but only indefinite products were obtained. Aqueous alcoholic potash converts acetone-chloroform into α-hydroxyisobutyric acid (m. p. 79°); potassium anilide converts it into phenylcarbylamine and acetone; with iodine and potassium hydroxide, carbonic oxide, potassium formate, iodide, and chloride, iodoform and water are formed; the action of bromine is similar to that of iodine; that of sulphur at 270° produces organic sulphur compounds. The action of methyl iodide in the presence of sodium, and of zinc ethide, produced no definite results. The action of ethyl sodacetoacetate produces three *compounds*: $C_{10}H_{17}O_5Cl$ = OH·CMe$_2$·CCl(CH$_2$·COOEt)·CH$_2$·COOH, an oil which boils at 175—178°; $C_{14}H_{24}O_7$ = OH·CMe$_2$·C(CH$_2$·COOEt)$_2$·CH$_2$·COOH, slender needles melting at 62°; $C_{10}H_{16}O_7$ = OH·CMe$_2$·C(CH$_2$·COOH)$_3$, an oil.

Asymmetrical dimethyltetraphenylethane, CPh$_3$·CMe$_2$Ph, is obtained by dissolving chlorisobutyric trichloride (20 grams) in excess of benzene and decomposing it with aluminium chloride; the reaction-mass is decomposed with water, distilled, and redistilled. This hydrocarbon is a pale yellow, aromatic oil boiling at 272°.

Tetramethylhexaphenylethyl ether, O(CMe$_2$·CPh$_3$)$_2$, is obtained by heating a mixture of "acetone-chloroform ether," aluminium chloride, and a large excess of benzene for four days in a reflux apparatus. It is an aromatic oil which boils at 262° (uncorr.).

A *compound*, $C_{10}H_{17}Cl_3O_3$, is obtained when "acetone-chloroform ether" is heated with alcoholic potash in a reflux apparatus; it is an oil which boils at 166° (uncorr.).

A. G. B.

Derivatives of Furfuracrylic Acid. By H. B. GIBSON and C. F. KAHNWEILER (*Amer. Chem. J.*, **12**, 314—325).—*Methyl furfuracrylate*, $C_7H_5O_3Me$, is prepared by treating carefully dried silver furfuracrylate with excess of methyl iodide, exhausting the product

with ether, and purifying by distillation under reduced pressure. It distils unchanged at 112° under a pressure of 15 mm., and the distillate, on cooling, solidifies to beautiful, rhombic crystals, which melt at 27°, dissolve readily in alcohol and ether, and have a characteristic odour.

Furfuracrylamide, $C_7H_5O_2 \cdot NH_2$, is obtained when methyl furfuracrylate is heated at 100° in sealed tubes with aqueous ammonia. It is sparingly soluble in cold water, and crystallises from hot water in pearly scales melting at 168—169°.

Bromofurfurodibromopropionic acid, $C_7H_5Br_3O_3$, is formed when furfuracrylic acid (1 mol.), suspended in carbon bisulphide, is treated with dry bromine (2 mols.). It crystallises in small, flat, oblique prisms, which are sparingly soluble in cold benzene and carbon bisulphide, but readily dissolve in alcohol and ether. When the acid is allowed to remain suspended in water for some time, carbonic anhydride escapes, and the crystalline solid is converted into *bromofurfurobromethylene*, a colourless oil, which, on treatment with alcoholic potash, gives the corresponding acetylene-derivative, a substance which cannot be readily purified, but forms with ammoniacal silver a white, and with ammoniacal copper a green, insoluble, metallic derivative. The latter, on oxidation with potassium ferricyanide, gives rise to *dibromodifurfurodiacetylene*, $C_4H_2BrO \cdot C \vdots C \cdot C \vdots C \cdot C_4H_2BrO$, a compound dissolving readily in all ordinary solvents except water, and crystallising from alcohol in small, iridescent plates melting at 126°.

Bromofurfuracrylic acid is obtained by treating an alcoholic solution of bromofurfurdibromopropionic acid with zinc-dust, which removes the bromine attached to the side chain only. It crystallises in long, slender prisms, which are sparingly soluble in cold water, more readily soluble in hot water, and dissolve readily in other common solvents, except light petroleum. It melts sharply at 176—177°, but is somewhat blackened by long-continued heating at temperatures above 150°, may be readily sublimed, and on treatment with bromine forms the original substituted propionic acid. The barium salt, $Ba(C_7H_4BrO_3)_2 + H_2O$, is sparingly soluble in cold water, and crystallises from hot water in clusters of needles; the calcium salt, $Ca(C_7H_4BrO_3)_2 + 3H_2O$, crystallises from hot water in columnar aggregations of plates; the sodium salt crystallises from cold water, in which it is readily soluble, in anhydrous nodular aggregates; the silver salt, $C_7H_4BrO_3Ag$, is nearly insoluble in water, and seems to be amorphous; the ethyl salt, $C_7H_4BrO_3Et$, crystallises from light petroleum in large, flat prisms melting at 42°.

Bromofurfurobromacrylic Acid.—The ammonium salt of this acid is formed by heating bromofurfurodipropionic acid in shallow vessels at 130°, boiling the residue with dilute ammonia, treating the solution with charcoal, and allowing it to crystallise. It forms sparingly soluble masses consisting of slender, felted needles, and on treatment with a dilute acid, yields the free acid, which crystallises in fine needles, melts at 178—179°, and may be readily sublimed. The barium salt, $Ba(C_7H_3Br_2O_3)_2 + 2H_2O$, is only sparingly soluble in boiling water, and forms lustrous scales; the silver salt is an amorphous powder; the potassium salt, $KC_7H_3Br_2O_3$, crystallises from hot

water in clusters of slender needles; the ethyl salt, $EtC_7H_3Br_2O_3$, crystallises from light petroleum in radiated groups of needles which melt at 55·–56°.

The analogies offered by the derivatives of pyromucic and cinnamic acids suggest the following constitutional formulæ for the above described compounds:—For bromofurfurodibromopropionic acid,

$$\begin{matrix} CH\cdot CH \\ \| \\ CBr\cdot O \end{matrix}\!\!>\!C\cdot CHBr\cdot CHBr\cdot COOH;$$

for bromofurfurobromethylene, $\begin{matrix} CH\cdot CH \\ \| \\ CBr\cdot O \end{matrix}\!\!>\!C\cdot CH\!:\!CHBr$; for bromofurfurobromacrylic acid, $\begin{matrix} CH\cdot CH \\ \| \\ CBr\cdot O \end{matrix}\!\!>\!C\cdot CH\!:\!CBr\cdot COOH$; and for bromofurfuracrylic acid, $\begin{matrix} CH\cdot CH \\ \| \\ CBr\cdot O \end{matrix}\!\!>\!C\cdot CH\!:\!CH\cdot COOH$.

G. T. M.

Condensation of Benzene and Acetylene under the Influence of the Silent Discharge. By P. SCHUTZENBERGER (*Compt. rend.*, **110**, 889—892; compare this vol., pp. 691, 692).—The tubes containing the benzene and acetylene were hermetically sealed, and thus the contents were cut off from any possible absorption of moisture from the air. It was found that after the discharge had been continued for five or six hours, the inner tube was very liable to break, a result due, according to the author, to the fact that the prolonged action of the discharge makes the glass brittle. If the tubes are quite vacuous, fracture takes place after a very few minutes.

Under the influence of the discharge, benzene vapour gradually condenses to a pale-yellow, resinous, transparent solid, the liquid benzene gradually disappearing. The product contains C, 85·9 to 91·63; H, 7·1 to 7·81; O, 0·7 to 7·0 per cent. The oxygen could not have been absorbed during the short time between opening the tube and weighing the substance; in fact, although the product does absorb oxygen from the air, the increase in weight is only 1 to 2 milligrams in more than an hour. Moreover, the composition of the product depends on whether it is formed on the inner tube or the outer tube.

	C.	H.	O.
Inner tube	90·54	7·30	2·10
Outer tube	87·14	7·48	5·38

The results agree with those obtained with acetylene, which gives a product containing 2 to 5 per cent. of oxygen. In one experiment, after 250 c.c. of acetylene had been almost completely condensed over mercury, hydrogen was introduced, and the passage of the spark continued. A reduction of volume ensued equal to the volume of acetylene remaining, and the contraction then ceased. The product contained C, 75·0; H, 8·9; O, 16·1 = 100, a result which, from the quantity of acetylene used, indicates that 0·02 gram of water had passed through the glass. The product did not absorb oxygen from the air. The glass was not affected.

C. H. B.

The Second Monobromobenzene. By F. FITTICA (*Ber.*, **23**, 1398—1400).—A reply to the paper of A. Hand (this vol., p. 881) on this subject. The author gives details of the method he employed for the preparation of the compound, to which he assigned the formula $(PhBr)_2,C_6H_6$. J. B. T.

Preparation of Phenyl Cyanate. By B. KÜHN and M. LIEBERT (*Ber.*, **23**, 1536—1537).—Phenylthiocarbimide (50 grams = 1 mol.) was heated at 170° in a reflux apparatus with well dried red oxide of mercury (80 grams = 1 mol.) mixed with some coarse glass powder. After heating for eight hours, the liquid was fractionated; the portion coming over below 170° was pure phenyl cyanate, and amounted to 20 per cent. of the theoretical yield; the rest was unattacked phenylthiocarbimide. If a larger proportion of mercuric oxide is used, the yield is lessened. C. F. B.

Action of Lead Oxide on Toluene. By C. VINCENT (*Compt. rend.*, **110**, 907—908).—When toluene is allowed to fall drop by drop on lead monoxide heated to a few degrees below its melting point (335°), the lead is reduced to the metallic state, carbonic anhydride is given off, and about 10 per cent. of benzene is formed, together with a very small quantity of stilbene, and higher products, $C_6H_5{\cdot}CH_3 + 3PbO = 3Pb + C_6H_6 + CO_2 + H_2O$.

At the melting point of the lead oxide, very little benzene is formed, and the product consists chiefly of stilbene mixed with oily hydrocarbons, the principal reaction being $2C_6H_5{\cdot}CH_3 + 2PbO = C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_5 + 2H_2O + 2Pb$.

At incipient redness, diphenyl, phenanthrene, anthracene, and other pyrogenic derivatives of benzene and toluene are obtained, together with the preceding products. C. H. B.

Nitration of Propylbenzene. By R. LESPIEAU (*Bull. Soc. Chim.* [3], **3**, 502—503).—From the liquid resulting from the action of a boiling mixture of nitric and sulphuric acids on propylbenzene or isopropylbenzene for several hours, small crystals of paranitrobenzoic acid separate on cooling. The liquid contains oily products which decompose even when distilled under reduced pressure, but by steam distillation, a nitropropylbenzene is obtained. By prolonged nitration of propylbenzene or isopropylbenzene, a mixture of dinitro-acids melting at 176°, and containing much 1 : 2 : 4-dinitrobenzoic acid, is formed. T. G. N.

Behaviour of Sodiophenylmercaptide with Isobutylene Bromide. By R. OTTO (*Ber.*, **23**, 1051—1052).—When isobutylene bromide is treated with sodiophenylmercaptide, phenyl bisulphide, isobutylene, and sodium bromide are formed; trimethylethylene bromide seems to behave in a similar manner. F. S. K.

Synthesis of Ketones from Phenol Ethers by Friedel and Crafft's Method. By L. GATTERMANN, R. EHRHARDT, and H. MAISCH (*Ber.*, **23**, 1199—1210).—As already shortly mentioned (Abstr., 1889,

862), acid chlorides react with phenol ethers in presence of aluminium chloride in just the same way as with the aromatic hydrocarbons, resembling in this respect phenyl cyanate and chloroformamide. The reaction is carried out by mixing the phenol ether and chloride in equivalent proportions (unless the chloride is very volatile, in which case an excess of that constituent is taken), adding carbon bisulphide as a diluent, and then gradually adding a quantity of aluminium chloride equal to $1\frac{1}{2}$ times or twice the quantity of phenol ether. The reaction is carried out in the cold, but may, if necessary, be started by gently warming. After allowing the mixture to remain for an hour, during which time it is frequently shaken, it is warmed for a few minutes on the water-bath, and the upper layer then poured off. The black aluminium double compound is washed with carbon bisulphide, and very carefully decomposed by water, the ketone separating as an oil or in crystals. In the latter case, it is simply filtered off and recrystallised from hot water, but in the second, it must be first taken up with ether, the ether evaporated off, and the residue purified either by distillation, or allowing it to remain until it crystallises.

Anisoïl and acetic chloride yield an oil, which on treatment with alcohol leaves a small quantity of dimethoxydiphenylethylene, $C_2H_2(C_6H_4{\cdot}OMe)_2$. After evaporating off the alcohol from the filtrate, the residual oil is distilled. The fraction boiling at 250—275° solidifies on cooling almost entirely, and is separated from the adhering oil by spreading on a porous plate, and recrystallising from ether. It then forms large, tabular crystals, melting at 38—39°, and boiling without decomposition at 258°. The analysis showed that *acetylanisoïl*, $C_6H_4Ac{\cdot}OMe$, had been formed. It unites with phenylhydrazine and hydroxylamine, forming crystalline derivatives, and, like many of the ketones to be described, gives very characteristic colour reactions with concentrated mineral acids. Thus, with concentrated sulphuric acid, it forms a deep, yellowish-red coloration, and with nitric acid, gives a magenta tint. On warming with the latter, it yields a substance probably belonging to the group of "nitro-sacyls" discovered by Hollemann. On oxidation acetylanisoïl yields anisic acid, showing that, as in the case of phenyl cyanate and chloroformamide, substitution has taken place in the para-position. The *paracetylanisoïl* described by Olivieri (*Gazzetta*, **13**, 275) as boiling at 220—222° must either have been impure, or have a different constitution.

Propionic chloride and anisoïl yield also a disubstituted propylene in small quantity, but the chief product is *parapropionylanisoïl*, $COEt{\cdot}C_6H_4{\cdot}OMe$. This forms colourless tablets which melt at 27°, and boil at 273—275°. It also yields anisic acid on oxidation, and forms an oxime, which crystallises from alcohol in colourless needles melting at 67°.

Benzoic chloride and anisoïl yield parabenzoylanisoïl, which forms large crystals melting at 61—62°. This compound has been previously obtained by Rennie by the oxidation of parabenzoylphenyl methyl ether (Trans., 1882, 220).

Phenetoïl combines with acetic chloride forming *acetylphenetoïl*, $C_6H_4Ac{\cdot}OEt$, which crystallises in six-sided tablets melting at 60—61°,

and yields parethoxybenzoic acid on oxidation. Phenetoïl and propionic chloride yield *propionylphenetoïl*, $COEt \cdot C_6H_4 \cdot OEt$, melting at 30°. Its oxime melts at 97°. Isobutyric chloride forms *isobutyrylphenetoïl*, which also forms a crystalline oxime, the melting points of the two compounds being 41° and 110—111° respectively. Benzoic chloride yields *parabenzoylphenetoïl*, which crystallises from acetic acid in silky plates melting at 38—39°, and distils above 300° without decomposition.

Resorcinyl diethyl ether is also acted on in the same manner by acetic and propionic chlorides, *acetylmetadiethoxybenzene* and *propionylmetadiethoxybenzene* being produced. The former crystallises in large, slightly pink needles melting at 67—68°, which give a beautiful green coloration with nitric acid. The second compound forms large, lustrous crystals melting at 76°, and yields an oxime melting at 133°. In neither of these cases is any unsaturated compound formed.

In addition to the above, the following compounds have been obtained from the corresponding naphthol ethers:—*Acetyl-α-naphthyl methyl ether*, crystallising in six-sided tables which melt at 71—72°, the acetyl group probably occupying the para-position; *propionyl-α-naphthyl methyl ether*, forming large prisms which melt at 58°, and yield an oxime melting at 172°; *acetyl-α-naphthyl ethyl ether*, crystallising in prisms which melt at 78—79°; *benzoyl-α-naphthyl ethyl ether*, melting at 74—75°; *acetyl-β-naphthyl methyl ether*, which forms slender, colourless needles melting at 57—58°; and, finally, *acetyl-β-naphthyl ethyl ether*, crystallising in large tables which melt at 62—63°.

In all these cases, the crystals are sufficiently large for the measurement of the angles, and might perhaps afford material for an examination of the relation between crystalline form and constitution. The same rule also appears to hold as in the case of phenyl cyanate and chloroformamide, namely, that substitution takes place in the para-position, unless that is previously occupied. In certain cases, an unsaturated alkylene compound is also formed. H. G. C.

Hexachlor-α-diketohexene. By T. ZINCKE (*Ber.*, **23**, 1334—1338).—Like the corresponding tetrachlororthoquinone, chloranil only takes up 2 atoms of chlorine on treatment with that reagent, forming a compound which has probably the formula $\begin{matrix} CCl \cdot CO \cdot CCl_2 \\ \| \qquad\qquad | \\ CCl \cdot CO \cdot CCl_2 \end{matrix}$, and may be termed for the present hexachlor-α-diketohexene. It is a colourless compound, insoluble in water, readily soluble in alcohol and ether, and melts at 88°. On further heating at the ordinary pressure, it loses chlorine, but may be distilled unchanged under diminished pressure. On reduction it yields tetrachloroquinol, and on energetic treatment with phosphorus pentachloride forms hexachlorobenzene. Less energetic treatment converts it into a compound containing phosphorus and chlorine, which is decomposed by water with formation of the compound $C_6Cl_5 \cdot OPO(OH)_2$, which may also be obtained in a similar manner from chloranil. On treatment with sodium hydroxide, it is converted into dichloromaleic acid, and an oily compound, probably tetrachlorethane. Contrary to the statement of

Kauder (Abstr., 1885, 652), and Ciamician (Abstr., 1884, 293), dichloromaleic acid, although extremely soluble in water, is not hygroscopic.

By the action of aniline, the compound $\begin{array}{l}CCl_2\cdot CO\cdot C\cdot NHPh \\ \mid \qquad\qquad \parallel \\ CCl_2\cdot CO\cdot CCl\end{array}$ is formed; it is a red, crystalline substance melting at 144°, and is converted by reduction into anilidotrichloroquinone. On treatment with alkali, it yields the sodium salt of an acid having the formula $C_{12}H_6Cl_3NO_3$, which readily loses carbonic anhydride, forming an indifferent compound of the formula $C_{11}H_6Cl_3NO$. As it also contains the phenyl-group, its formula may be written $C_5Cl_3NOPh\cdot COOH$. It appears probable that by the action of the alkali the ring is split, with formation of the compound $CCl_2{:}CCl\cdot CO\cdot CCl{:}C(NHPh)\cdot COOH$, and that this loses another molecule of hydrogen chloride, forming *phenyltrichloropyridonecarboxylic acid*, $\begin{array}{l}CCl\cdot NPh\cdot C\cdot COOH \\ \parallel \qquad\qquad \parallel \\ CCl\cdot CO\cdot CCl\end{array}$. This melts at 245° with evolution of carbonic anhydride, and is soluble without decomposition in hot water, cold alcohol, and cold soda solution. On heating with the latter, one chlorine-atom is replaced by hydroxyl, forming *phenyldichlorohydroxypyridonecarboxylic acid*, $OH\cdot C_5NPhCl_2O\cdot COOH$, melting at 206°, which yields a *dimethyl* salt, and a *silver* salt containing two atoms of silver. On boiling with acetic anhydride, it loses carbonic anhydride, and forms *acetylphenyldichlorohydroxypyridone* melting at 143°. The indifferent compound $C_{11}H_6Cl_3NO$, or *phenyltrichloropyridone*, melts at 245°.

Methylamine also readily acts on hexachloro-α-diketohexene, but the compound obtained is colourless, and has quite different properties to the anilide. It is now being more closely investigated.

H. G. C.

A New Hydroxythymoquinone. By G. Mazzara (*Ber.*, **23**, 1390—1392).—Two hydroxythymoquinones are theoretically possible, namely, [Me : OH = 1 : 2] and [Me : OH = 1 : 5]. The former of these, the α-compound, melting at 166—167°, has long been known; the latter, the β-compound, is obtained by reducing dinitrocarvacrol and oxidising the product with ferric chloride. The quinone is purified by distillation in a current of steam; it crystallises from dilute alcohol in long, prismatic, dark orange-yellow plates, melting at 181—183°. Hydroxythymoquinone dissolves in alkaline carbonates, the solution becoming violet in colour. J. B. T.

Safrole. By G. Ciamician and P. Silber (*Ber.*, **23**, 1159—1164).—In the course of their investigation of apiole, it appeared to the authors advisable to examine also the properties of the analogous compounds safrole and methyleugenol. Some of the results given in this paper have also been recently published by Eykman (this vol., p. 748) in agreement with whom the authors find that the isafrole obtained by Poleck (Abstr., 1884, 1339) and Schiff (Abstr., 1884, 1338), by the action of sodium and solid potassium hydroxide on safrole under pressure, may be more readily prepared by warming safrole with alcoholic potash. It forms an oil boiling at 246—248°,

remaining solid at $-18°$, miscible with alcohol, ether, and benzene, but insoluble in water and alkalis. Its molecular weight was found by Raoult's method to be 159, which agrees with the formula $C_{10}H_{10}O_2$. Like safrole, it dissolves in concentrated sulphuric acid with an intense red coloration.

With potassium dichromate and sulphuric acid, isafrole yields piperonal and acetaldehyde, the oxidation proceeding therefore in the same manner as with isapiole. Alkaline potassium permanganate, on the other hand, converts it into piperonylic acid, and a ketonic acid which appears to be *dioxymethylenephenylglyoxylic acid*,

$$CH_2{<}\genfrac{}{}{0pt}{}{O}{O}{>}C_6H_3{\cdot}CO{\cdot}COOH,$$

which may be shortly termed *piperonylketonic acid*. It crystallises from water in pale-yellow needles which melt at 148—149°, and from benzene in needles containing benzene of crystallisation melting at 130—140°, which do not lose all their benzene at 100°. It gives a yellow compound with phenylhydrazine. The *silver* salt, $C_9H_5AgO_5$, crystallises from hot water in lustrous prisms.

Whereas safrole is scarcely acted on by reducing agents, isafrole is readily converted by sodium in alcoholic solution into dihydrosafrole, an almost colourless liquid boiling at 228°, miscible with alcohol, ether, benzene, and acetic acid. It gives with concentrated sulphuric acid, first a yellow, and then a red coloration. It is in all probability formed by the addition of two hydrogen-atoms to the allyl-group, and would thus have the constitution $CH_2{<}\genfrac{}{}{0pt}{}{O}{O}{>}C_6H_3Pr^{\alpha}$. The aqueous alkaline solution contains a snbstance having the composition and properties of a propylphenol, corresponding closely with the metapropylphenol described by Jacobsen (Abstr., 1878, 732). It conld only be obtained, however, as a liquid, whereas Jacobsen gives its melting point as 26°.

Its methyl ether, which boils at 212—213° (corr.), yields on oxidation with alkaline potassium permanganate metamethoxybenzoic acid. It follows, therefore, that, on reduction, isafrole loses the atom of oxygen occupying the para-position.

Bromine acts on isafrole in carbon bisulphide solution, forming monobromisafrole dibromide, $C_{10}H_9BrO_2,Br_2$, which crystallises from light petroleum in colourless, lustrous needles melting at 109—110°.

H. G. C.

Eugenol. By G. CIAMICIAN and P. SILBER (*Ber.*, **23**, 1164—1167). —Unlike safrole (see preceding abstract) eugenol is not completely converted by alcoholic potash into an isomeride. The methyl ether, however, prepared by the action of methyl iodide and potash on eugenol, is readily and completely converted into isomethyleugenol. The first-named methyl ether boils at 247—248°, whilst the isomeride forms a colourless, almost odourless liquid boiling at 263°. On oxidation with sulphuric acid and potassium dichromate, it is converted into methylvanillin and veratric acid, whilst with alkaline potassium permanganate it yields the latter acid, and a new compound

which has the composition $C_{10}H_{10}O_5$, and crystallises from water in white, nodular aggregates or large needles melting at 137°. It is also soluble in alcohol, ether, acetic acid, and benzene, the crystals obtained from the latter containing benzene of crystallisation. It combines with phenylhydrazine, and is probably *dimethoxyphenylglyoxylic acid*, $(CH_3O)_2{\cdot}C_6H_3{\cdot}CO{\cdot}COOH$.

Like isapiole and isafrole, the methyl ether of isoeugenol readily takes up 2 atoms of hydrogen when treated with sodium in hot alcoholic solution. The hydromethyleugenol thus obtained is an oil resembling hydrosafrole in smell, which boils at 246°, and dissolves in concentrated sulphuric acid on warming, forming a pale-red solution.

Isomethyleugenol also combines with bromine forming *isomethyleugenol dibromide*, $C_{11}H_{14}Br_2O_2$, which crystallises from light petroleum in colourless crystals melting at 101—102°. It is soluble in ether, chloroform, and benzene, and insoluble in water, but melts on boiling with the latter, and imparts to it an acid reaction. H. G. C.

Diamidoquinol Ether and Dihydroxyquinone Ether. By R. NIETZKI and F. RECHBERG (*Ber.*, 23, 1211—1217).—It was shown 10 years ago, by Nietzki (Abstr., 1879, 464), that quinol diethyl ether, on treatment with nitric acid, yields a mixture of two dinitro-derivatives, which may be separated by their different solubility in acetic acid, alcohol, or ethyl acetate. As the α-compound gave on reduction a diamido-compound which could be readily converted into an azimido-derivative, it appeared probable that the nitro-groups in that compound occupied the ortho-position.

The re-examination of these compounds has shown that the dinitro-componnds may be readily reduced by a mixture of stannous chloride, concentrated hydrochloric acid, and alcohol, and the amido-compounds then obtained in the form of hydrochlorides by passing in hydrogen chloride, and decomposing the precipitated stannochloride with hydrogen sulphide. It was found that the β-compound may be readily obtained free from the α-compound, but the α-compound invariably contains small quantities of its isomeride.

α-Diamidoquinol diethyl ether hydrochloride forms large needles which become grey in the air. Nitrous acid readily converts it into the azimide previously described, and it also unites with diacetyl, benzile, and phenanthraquinone, forming quinoxalines melting at 127°, 163°, and 260° respectively. There can therefore be no doubt that the amido-groups occupy the ortho-position.

β-Diamidoquinol diethyl ether may be readily separated from the α-compound by adding sulphuric acid and alcohol to the mixture of their hydrochlorides, when the sulphate of the β-compound separates out in colourless needles. Both the hydrochloride and sulphate are converted by ferric chloride into a substance which crystallises in pale-yellow plates melting at 183°. It is free from nitrogen, and has the formula $C_{10}H_{12}O_4$, and on treatment with caustic potash is converted into the symmetrical dihydroxyquinone obtained by Nietzki and Schmidt from di-imidoresorcinol. The oxidation-product must therefore be the diethyl ether of this substance, and has the constitu-

tion $O_2 : OEt_2 = 1 : 4 : 3 : 6$. It follows, therefore, that β-diamidoquinol diethyl ether has also the symmetrical constitution.

When dihydroxyquinone diethyl ether is treated with stannous chloride, hydrochloric acid, and alcohol, it is converted into *tetrahydroxybenzene diethyl ether*, $C_6H_2(OH)_2(OC_2H_5)_2$, which crystallises from water in beautiful needles melting at 138°, and yields a diacetyl compound which melts at 148°. On treatment with the requisite quantity of sodium ethoxide and ethyl bromide or iodide, it forms *tetrethoxybenzene*, which crystallises in colourless, lustrous plates, melts at 143°, and sublimes very readily.

Dihydroxyquinone diethyl ether yields with hydroxylamine a dioxime which is as good as insoluble in all ordinary solvents, and melts above 300°.

The compound obtained by Habermann (Abstr., 1878, 728) by acting on quinol dimethyl ether with nitric acid has proved on examination to be a mixture of two isomeric dinitro-compounds, which may be separated by fractional crystallisation from ethyl acetate. The more readily soluble compound melts at 177°, and the second at 202°. The amido-derivatives obtained by Karioff by the reduction of Habermann's compound (Abstr., 1881, 272) must also be a mixture. The nitro-derivative melting at 177°, on reduction with stannous chloride, hydrochloric acid, and alcohol, yields a diamido-compound which shows all the properties of an ortho-derivative, combining with diacetyl, benzile, and phenanthraquinone to form quinoxalines.

The nitro-derivative melting at 202° on reduction gives a diamido-compound analogous in all respects to β-diamidoquinol diethyl ether, and which must therefore likewise have a symmetrical constitution. It is converted by ferric chloride into a dimethoxyquinone identical with the compound obtained by Nietzki and Schmidt by acting on the silver compound of dihydroxyquinone with methyl iodide. It is readily reduced by stannous chloride and hydrochloric acid with formation of tetrahydroxybenzene dimethyl ether, which forms small, lustrous plates melting at 166°.

The above results show that dihydroxyquinone really contains two hydroxyl-groups, and has not passed into the tautomeric tetraketohexamethylene, for the dimethyl ether obtained by direct methylation, and the compound formed from amidoquinol dimethyl ether are identical, and the latter undoubtedly contains two methoxy-groups.

H. G. C.

Derivatives of Ortho- and Para-tolubenzylamine. By T. Kröber (*Ber.*, **23**, 1026—1034).—Orthotolubenzylamine can be prepared by reducing orthotolunitrile with sodium and alcohol; it boils at 199·5° (corr.). The *benzoyl*-derivative, $C_6H_4Me{\cdot}CH_2{\cdot}NHBz$, crystallises from alcohol in needles, melts at 88°, and is soluble in most ordinary solvents except water.

Orthoditolubenzylthiocarbamide, $CS(NH{\cdot}CH_2{\cdot}C_6H_4Me)_2$, prepared by heating the amine with carbon bisulphide and alcohol, crystallises from dilute alcohol in colourless plates or prisms melting at 186—187°.

Diazobenzeneorthotolubenzylamine, $C_6H_4Me\cdot CH_2\cdot NH\cdot N_2\cdot Ph$, obtained by treating the amine with diazobenzene chloride in dilute alcoholic solution, crystallises from alcohol in almost colourless needles, melts at 85°, and is readily soluble in ether and chloroform, but only sparingly in dilute alcohol, and insoluble in water.

Orthotolubenzyl alcohol is obtained when the amine is treated with nitrous acid; it melts at 31°. The corresponding aldehyde boils at 198—200°.

Orthomethylcinnamic acid, $C_6H_4Me\cdot CH\!:\!CH\cdot COOH$, can be prepared by heating orthotolualdehyde with sodium acetate and acetic anhydride at 145—150°; it crystallises from benzene in needles, and melts at 169°.

Paratolubenzylamine (b. p. 195—196°) is formed when paratolunitrile is reduced with sodium and alcohol. The *mercurochloride* crystallises in colourless prisms and melts at 203°; the *picrate*, $C_8H_{11}N,C_6H_3N_3O_7$, separates from water in moss-like crystals, and melts at 194—199° with decomposition. The *benzoyl*-derivative, $C_6H_4Me\cdot CH_2\cdot NHBz$, crystallises from alcohol in long, colourless needles, melts at 125°, and is readily soluble in ether, but insoluble in water.

Paratolubenzylcarbamide, $C_6H_4Me\cdot CH_2\cdot NH\cdot CO\cdot NH_2$, prepared by treating the hydrochloride of the amine with potassium cyanate, crystallises from dilute alcohol in plates, and melts at 166°.

Di-paratolubenzylthiocarbamide, $CS(NH\cdot CH_2\cdot C_6H_4Me)_2$, crystallises in colourless plates melting at 124—125°.

Diazobenzeneparatolubenzylamine, $C_6H_4Me\cdot CH_2\cdot NH\cdot N_2Ph$, crystallises in colourless plates, melts at 60—61°, and is soluble in ether, alcohol, and light petroleum.

Paratolubenzylacetamide, $C_6H_4Me\cdot CH_2\cdot NHAc$, prepared by treating the amine with acetic chloride, is a colourless, crystalline compound melting at 106·5°.

Paramethylcinnamic acid, $C_6H_4Me\cdot CH\!:\!CH\cdot COOH$, prepared from paratolualdehyde, crystallises from benzene in colourless needles, melts at 197°, and is soluble in most ordinary solvents. The *dibromide*, $C_{10}H_{10}Br_2O_2$, crystallises from light petroleum in needles, and melts at 183°.

Paramethylhydrocinnamic acid, $C_{10}H_{12}O_2$, is formed when the preceding compound is reduced with sodium amalgam; it crystallises from hot water in plates, and melts at 120°. F. S. K.

Action of Orthodiamines on Phthalaldehydic Acid. By A. BISTRZYCKI (*Ber.*, 23, 1042—1046).—*Toluyleneamidinebenzenylorthocarboxylic acid*, $C_6H_3Me{<}{}^{N}_{NH}{>}C\cdot C_6H_4\cdot COOH$, separates as an orange precipitate when phthalaldehydic acid (benzaldehydeorthocarboxylic acid) is treated with orthotoluylenediamine in aqueous or alcoholic solution. It crystallises from alcohol in colourless needles, melts at 258° with decomposition, and is almost insoluble in water, chloroform, acetone, ether, and toluene, and only very sparingly soluble in boiling alcohol; it dissolves freely in glacial acetic acid and in mineral acids, and also in alkalis and alkaline carbonates.

Bromotoluyleneamidinebenzenylorthocarboxylic acid,

$$C_6H_2BrMe<\genfrac{}{}{0pt}{}{-N}{NH}>C\cdot C_6H_4\cdot COOH,$$

obtained from bromoparatolnylenediamine (see below), in like manner, melts at 267°.

Phenyleneamidinebenzenylorthocarboxylic acid,

$$C_6H_4<\genfrac{}{}{0pt}{}{-N}{NH}>C\cdot C_6H_4\cdot COOH,$$

prepared from orthophenylenediamine, decomposses at 266°. The corresponding *naphthalene*-derivative, $C_{18}H_{12}N_2O_2$, decomposes at about 280°.

These three compounds all form microscopic crystals, and are very sparingly soluble or insoluble in most neutral solvents.

Bromotoluylenediamine [$Me : (NH_2)_2 : Br = 1 : 3 : 4 : 5$] can be prepared by brominating metanitroparatoluidine in alcoholic solution and reducing the product with stannous chloride and hydrochloric acid; it crystallises in long needles, melts at 81—82° with previous softening, and is very readily soluble in alcohol, ether, chloroform, acetone, and benzene, but only sparingly in water. F. S. K.

Stereochemically Isomeric Nitrogen Compounds. By A. HANTZSCH and A. WERNER (*Ber.*, **23**, 1243—1253; compare this vol., p. 348).—In consequence of the work of Klinger and Zuurdeeg (this vol., p. 761) on the trinitroazotoluenes, the authors regard the existence of stereochemically isomeric azo-compounds as doubtful, and acknowledge that these can no longer be cited in support of their theory. In all other points the theory is upheld, and the objections raised by V. Meyer with regard to the isomeric oximes (this vol., p. 719) are replied to. The authors point out that if Beckmann's isobenzaldoxime had the constitution $\begin{array}{c}Ph\cdot C\cdot NH\\ \diagdown\diagup\\ O\end{array}$, it would be intermediate between $Ph\cdot CH\colon NOH$ and $Ph\cdot CO\cdot NH_2$, and might, therefore, be expected to readily undergo change into the latter, which is not the case. They are, therefore, still of opinion that the structure of the isomeric benzaldoximes is similar. The fact that Auwers fails to discover an isomeride of the unsymmetrical oxime of the formula $OH\cdot N\colon CPh\cdot C_6H_4Me$ cannot be taken as any positive proof against the theory, for reasons which the authors have already given in their former paper. The absence of isomeric oximes of phenanthraquinone may, perhaps, be explained by the total difference in structure between this compound and benzile, the former containing a closed ring, which is not the case with the latter, and therefore having an essentially different structure. H. C.

Diazo-compounds. By L. GATTERMANN, W. HAUSSKNECHT, A. CANTZLER, and R. EHRHARDT (*Ber.*, **23**, 1218—1228).—Experiments made by the authors with the object of obtaining diphenyl from diazobenzene chloride by the action of finely-divided copper had not

the desired result, but led to the formation of chlorobenzene. Further investigation has shown that finely-divided copper exerts generally an action on diazo-salts very similar to that of cuprous salts discovered by Sandmeyer. The new reaction has, however, many advantages over the latter method, as it takes place in the cold, and it is unnecessary to prepare a special salt containing the residue to be introduced into the benzene nucleus, it being sufficient to add copper powder and a solution of the potassium or sodium salt of the acid.

The results obtained up to the present may be divided into three groups:—

(1.) Replacement of the amido-group, by halogens, thiocyanogen, and cyanogen. The copper powder was prepared by adding zinc-dust to a saturated solution of copper sulphate until the latter has only a pale-blue colour, washing the precipitated copper by decantation, and treating with dilute hydrochloric acid to remove traces of zinc. After filtering and washing, the paste of copper powder should be placed in a well-closed bottle, as it readily undergoes oxidation.

For the preparation of chlorobenzene, aniline is diazotised in the usual manner, using an excess of acid, and the copper powder gradually added, with constant stirring; nitrogen is rapidly evolved, and the reaction is complete in 15—30 minutes. The aqueous solution is poured, as completely as possible, from the lower oily layer, and the latter distilled in a current of steam. The distillate consists of chlorobenzene and a little diphenyl.

Ortho- and para-toluene in the same manner form ortho- and para-chlorotoluene, the yield being in both cases considerably better than that given by Sandmeyer's method. β-Naphthylamine is also readily converted into β-chloronaphthalene, but a large quantity of resinous matter is also formed, the yield of pure substance being only 30 per cent. Parachloronitrobenzene has also been prepared by this method from paranitraniline.

Metachlorobenzaldehyde may be prepared from metanitrobenzaldehyde by reducing the latter with stannous chloride and hydrochloric acid, diazotising directly without removing the tin, and adding copper powder.

For the preparation of bromobenzene, aniline is diazotised by means of sulphuric acid and sodium nitrite, and mixed with an aqueous solution of potassium bromide. The copper powder is then gradually added, the appearances being the same as with the chlorine compound. On distilling in a current of steam, almost pure bromobenzene is obtained. Iodobenzene and para-iodotoluene can be prepared in an exactly similar manner. The cyanogen- and thiocyanogen-groups can also be thus substituted for the amido-group, but the reactions have not as yet been closely studied.

(2.) Replacement of the amido-group by the cyanic acid residue. —The potassium cyanate required was prepared according to the method of C. A. Bell (this Journal, 1876, i, 68), by heating a mixture of potassium ferrocyanide and potassium dichromate, and extracting the product with 80 per cent. alcohol. A concentrated aqueous solution of the salt (9 grams) was added to a solution of 10 grams of aniline, diazotised in the usual manner, and then the copper added in

portions of 5 grams, with constant stirring, until no more nitrogen is evolved. The phenyl cyanate forms an oily layer on the surface, and is removed by means of a glass spoon as it is formed, ether added, the water taken with it separated, and the ethereal solution dried over ignited potassium carbonate, evaporated, and distilled. The phenyl cyanate thus obtained contains a little coloured impurity, which has not yet been removed, but which is not retained by the derivatives obtained from the phenyl cyanate, such as phenyl- and diphenyl-carbamide. A residue is also obtained from the distillation of the phenyl cyanate, probably consisting of phenyl phenylcarbamate, NHPh·COOPh.

Orthotolyl cyanate may also be obtained in this manner from orthotoluidine, the yield being better than in the foregoing case.

(3.) Conversion of aniline into diphenyl.—For this purpose aniline is diazotised with sulphuric acid and sodium nitrite, and a quantity of 90 per cent. alcohol added. Copper powder is then gradually introduced, and the mixture vigorously stirred for an hour. The whole is then distilled in a current of steam, and the distillate collected as soon as it gives a solid precipitate on addition of water. The diphenyl thus obtained is perfectly pure. Concerning the mechanism of the action, all that is known at present is that the alcohol is partially oxidised to aldehyde, and the copper also oxidised to some extent. The copper may be replaced by finely-divided zinc or iron.

Culmann and Gasiorowsky have also recently obtained diphenyl from diazobenzene chloride by the action of stannous chloride, but the action is more complicated. Better results were obtained by the action of stannous chloride on diazobenzene formate in presence of formic acid (Abstr., 1889, 1156), but the copper method is preferable as being much cheaper. H. G. C.

Piazothioles and Piaselenoles II. By O. HINSBERG (*Ber.*, 23, 1393—1397; compare Abstr., 1889, 785, and this vol., p. 160).—1 : 2-Naphthylenediamine, obtained by the reduction of benzeneazo-β-naphthylamine, yields *naphthapiazothiole*, $C_{10}H_6N_2S$, when heated to 180—200° for 6 to 8 hours with hydrogen sodium sulphite in a sealed tube. The products of the reaction are treated with dilute hydrochloric acid, and distilled in a current of steam. Naphthapiazothiole crystallises from methyl alcohol in colourless or slightly yellow needles or leaves, melting at 81°. It is a feeble base, and gives a yellow coloration with concentrated sulphuric acid; with tin and hydrochloric acid, it yields naphthylenediamine and hydrogen sulphide.

1 : 2-*Naphthaquinoxaline*, $C_{10}H_6{:}C_2N_2H_2$, is obtained by warming a mixture of 1 : 2-naphthalenediamine and glyoxal hydrogen sodium sulphite with acetic acid; after purification, the compound crystallises from dilute alcohol in small, colourless needles, melting at 62°; its salts are yellow in solution, and are not dissociated. The *platinochloride* is sparingly soluble in water. The base is stable towards oxidising agents and nitrous acid; concentrated sulphuric acid produces a deep-red coloration, which changes to yellow on the addition of water.

Experiments made with the object of ascertaining what influence, if any, the presence of alkalis or acids exerts on the formation of piaselenoles, show that alkaline selenites do not react with 1 : 3 : 4-diamidotoluene, and that dilute mineral acids do not affect the ordinary course of the reaction. On warming a mixture of equal molecular parts of 1 : 3 : 4-diamidotoluene and selenious anhydride in concentrated hydrochloric acid, the solution becomes yellowish-red in colour, and a considerable quantity of crystals are deposited which chiefly consist of *methylchloropiaselenole*, $C_6H_2ClMe:N_2Se$, melting at 149—150°. This compound shows all the characteristic properties of the piaselenoles; it is a feeble base, gives a yellowish-red colour with concentrated sulphuric acid, and, on reduction, yields a chlorodiamidotoluene. As selenious anhydride and concentrated hydrochloric acid have no action on methylpiaselenole, the above reaction is probably best explained by assuming that the compound $SeCl_2(OH)_2$ is first formed, and that this then unites with the diamidotoluene, giving the compound $C_7H_6{<}{}^{NH}_{NH}{>}SeCl_2$; by the loss of two hydrogen-atoms, the dichloride, $C_7H_6:N_2SeCl_2$, would be produced, from which methylchloropiaselenole is finally obtained by elimination of hydrogen chloride and atomic rearrangement. Selenic acid combines with diamidotoluene to form methylpiaselenole, part of the amine being simultaneously oxidised to a red-coloured compound. J. B. T.

Formation of Alkyl-derivatives of Amides. By J. TAFEL and C. ENOCH (*Ber.*, **23**, 1550—1554; compare this vol., p. 491).—*Silver metanitrobenzamide*, $C_7H_5N_2O_3Ag$, prepared by dissolving metanitrobenzamide in dilute alcohol, precipitating with silver nitrate and soda, and carefully drying, is a grey powder, which by heating for several days at 50° with ethyl iodide, extracting the mass with ether, and precipitating by the addition of ethereal hydrogen chloride to the ether extract, yields the *hydrochloride of metanitrobenzimidoethyl ether*, $NO_2\cdot C_6H_4\cdot C(OEt):NH,HCl$. It forms a horny mass soluble in alcohol and water; when the aqueous solution is warmed, decomposition ensues, ammonia and ethyl metanitrobenzoate, melting at 43° (uncorr.), being formed. *Metanitrobenzimidoethyl ether* was prepared by dissolving the hydrochloride in water, and adding the calculated quantity of sodium carbonate. It is an uncrystallisable oil, but its acid oxalate, $C_{11}H_{12}N_2O_7$, forms well-developed crystals. *Metanitrobenzamidine hydrochloride*, $NO_2\cdot C_6H_4\cdot C(NH)\cdot NH_2,HCl$, was prepared from it by Pinner's method (Abstr., 1883, 1089); it dissolves easily in water, less easily in alcohol, and is precipitated from solution in the latter solvent by the addition of ether, in white tables melting at 240°. The *platinochloride* forms small, glittering, yellowish plates. Free *metanitrobenzamidine* was obtained by decomposing the hydrochloride with excess of soda; it forms ill-defined crystals which are soluble in water and have a strongly alkaline reaction.

When mercury-acetamide is suspended in ether and mixed with iodine, a brick-red powder of the constitution $HgI_2(NHAc)_2$ is formed; when this is dissolved in hot alcohol and the solution cooled, it separates as an oil, but soon solidifies to a crystalline mass. It is

insoluble in benzene, is decomposed by heat, and by dilute hydrochloric acid, but not by other dilute acids.

When mercury-benzamide is treated in the same way, a similar red powder, $HgI_2(NHBz)_2$, is formed. When this is boiled with alcohol, it is decomposed into two componnds, one not containing merenry, probably C_7H_6NOI, the other C_7H_6NOHgI, obtained in small, white needles melting at 194°, and decomposing at a higher temperature; it is insoluble in water.

When silver-carbamide, $CON_2H_2Ag_2$, is treated with iodine in the above manner, a greenish mass of $CON_2H_2Ag_2I$ is formed, extremely sensitive to light, and decomposed with liberation of silver iodide when heated alone or with alcohol, some aldehyde being formed in the latter case. Dilute hydrochloric acid liberates the iodine.

C. F. B.

A Modification of the Chloroformamide Synthesis. By L. GATTERMANN and A. ROSSOLYMO (*Ber.*, **23**, 1190—1199).—About two years ago, one of the authors, in conjunction with G. Schmidt, W. Hess, and E. P. Harris, described a new method of synthetically preparing aromatic carboxylic acids, which consisted in acting with chloroformamide on aromatic hydrocarbons and phenol ethers in presence of aluminium chloride (Abstr., 1887, 569; 1888, 574). For the preparation of chloroformamide in quantity, a considerable quantity of condensed carbonyl chloride is necessary, which is not always readily obtained, and moreover, the time required in the preparation of the chloroformamide is too great in comparison with the actual preparation of the carboxylic acid, when only small quantities of the latter are required. The authors have succeeded in effecting a modification of the method by which the difficulties in the preparation of small quantities have been successfully overcome. Led by the fact that chloroformamide, which appears to distil unchanged, really splits up into cyanic acid and hydrogen chloride, they have examined the effect of replacing the chloroformamide by a mixture of cyanic acid and hydrogen chloride, and find that the mixture acts in exactly the same way with the aromatic hydrocarbons and phenol ethers.

For the preparation of cyanic acid, cyanuric acid is recrystallised from water, the hydrated crystals carefully heated until anhydrous, and the acid then distilled in a suitable vessel, passing a current of carbonic anhydride through it during the operation. The vapours are led into a wide necked flask, into which also passes a tube conveying hydrogen chloride. In the flask is placed a quantity of powdered aluminium chloride equal to that of the cyanuric acid taken, and the hydrocarbon or phenol ether to be acted on, the latter being diluted with carbon bisulphide if the quantity is small, and it is to be couverted as fully as possible into the amide. Through a third hole in the flask is placed a fairly wide tube, which serves to condense the carbon bisulphide boiled off during the reaction. The whole is gently warmed, and the cyanic acid vapours mixed with carbonic anhydride, and the hydrogen chloride simultaneously passed in, the flask being continually shaken. After the reaction is over, the liquid is poured off from the solid or semi-solid aluminum double salt, and the latter

carefully decomposed with water, cooling well during the operation. The amide usually separates at once or, if the quantity is small, may be extracted with ether, and then crystallised from hot water after treatment with animal charcoal.

Benzene gives the worst yield of any of the hydrocarbons. The compound obtained crystallises in colourless plates melting at 128°, and is identical in every respect with benzamide. Even with a small quantity of benzene and an excess of cyanic acid and hydrogen chloride, the yield is not good.

Toluene, under the same conditions, gives a much better yield of paratoluamide, melting at 158°. As with phenyl cyanate and chloroformamide itself, the hydrogen-atom occupying the para-position to the methyl-group is replaced. Ethylbenzene yields the previously unknown *parethylbenzamide*, $C_6H_4Et{\cdot}CO{\cdot}NH_2$, which is sparingly soluble in hot water, and crystallises from it in colourless plates melting at 115—116°. The acid obtained from it by hydrolysis is identical with parethylbenzoic acid.

Metaxylene is converted by the reaction into *metaxylylamide*, $C_6H_3Me_2{\cdot}CO{\cdot}NH_2$ (1 . 3 . 4), melting at 178—179°. By means of this reaction the authors have been able to ascertain that a sample of xylene from coal-tar consisted chiefly of metaxylene mixed with a little ethylbenzene.

Anisoïl readily yields anisamide, which crystallises in white needles and melts at 162—163°, and not at 137—138°, as given by Henry.

Pheuetoïl is also converted with great ease into the amide of ethoxybenzoic acid, crystallising in lustrous plates melting at 201°.

Naphthalene, acenaphthene, and α-naphthyl ethyl ether are also acted on by these reagents. The first yields the amide of α-naphthoic acid, melting at 201—202°, and the second an amide melting at 197—198°, whilst the third gives an amide for which the authors, in agreement with Hess, find the melting point 143—144°.

This reaction also permits of the detection of the constituents of a mixture of hydrocarbons. Thus, a mixture of toluene and metaxylene, treated with half the quantity of cyanic acid necessary to convert the whole into amide, yielded nearly pure metaxylylamide, and the residual hydrocarbon on further treatment yielded paratoluamide.

H. G. C.

Action of Carbonyl Chloride on Orthodiamines. By A. HARTMANN (*Ber.*, 23, 1046—1051. Orthophenylenecarbamide (m. p. 307—308°) is formed when carbonyl chloride is heated with orthophenylenediamine hydrochloride in toluene solution; orthotoluylenecarbamide (m. p. 291—292°), and orthonaphthyleneearbamide (m. p. about 380°) can be obtained in like manner.

Bromotoluylenecarbamide, $C_6H_2BrMe{<}{\genfrac{}{}{0pt}{}{NH}{NH}}{>}CO$, prepared from bromotoluylenediamine (m. p. 81—82°) melts at 324—325°, and is readily soluble in alcohol, but only sparingly in benzene, ether, and water.

Diacetylbromotoluylenediamine, $C_6H_2BrMe(NHAc)_2$, is obtained when bromotoluylenediamine [$Me : (NH_2)_2 : Br = 1 : 3 : 4 : 5$] is boiled with acetic anhydride; it crystallises from water in needles, melts at 222—223°, and is readily soluble in glacial acetic acid and

alcohol, but more sparingly in water, benzene, and toluene. The *monacetyl*-derivative, $C_9H_{11}BrN_2O$, can be prepared by reducing metanitrometabromoparacetotoluide with stannous chloride and hydrochloric acid in the cold; it separates from benzene in crystals and melts at 167—168°.

Ethenylbromotoluyleneamidine, $C_6H_2BrMe<\begin{smallmatrix}N\\NH\end{smallmatrix}>CMe$, is formed when acetyl- or diacetyl-bromotoluylenediamine is heated above its melting point, and also when nitrobromacetotoluide is reduced at a moderately high temperature; it crystallises from alcohol in prisms, melts at 197—198°, and is readily soluble in alcohol, but only sparingly in benzene and water.

Dibenzoylbromotoluylenediamine, $C_6H_2BrMe(NHBz)_2$, crystallises in colourless needles melting at 244°.

Diphenylbromotoluquinoxaline, $C_6H_2BrMe<\begin{smallmatrix}N:CPh\\ \vert \\ N:CPh\end{smallmatrix}$, prepared by boiling bromotoluylenediamine with benzile in alcoholic solution, crystallises in needles, and melts at 153—154°.

Bromotoluphenanthrazine, $C_{21}H_{13}BrN_2$, is formed when bromoparatoluylenediamine is treated with phenanthraquinone in glacial acetic acid solution; it crystallises from a mixture of chloroform and alcohol in yellow needles melting at 209—210°. F. S. K.

Derivatives of Trimethylenediamine. By A. GOLDENRING (*Ber.*, **23**, 1168—1174).—Aniline readily acts on γ-bromopropylphthalimide at 150°, aniline hydrobromide separating out. On addition of aqueous ammonia and distilling in a current of steam, an oil remains which may be purified by adding boiling water and concentrated hydrochloric acid, until all but a small quantity of resinous matter is dissolved. On cooling the filtered solution, the salt formed separates in white granules, which are reconverted into the base by warming with dilute aqueous ammonia; the product thus obtained is dissolved in a small quantity of benzene, and a large excess of alcohol added. The yellow crystals which separate, melt at 144—145°, and consist of *diphthalylditrimethylenetriamine* $NPh(CH_2\cdot CH_2\cdot CH_2\cdot N:C_8H_4O_2)_2$. On heating this compound with fuming hydrochloric acid in a sealed tube at 240°, it is converted into *di-trimethylenephenyltriamine hydrochloride*, $NPh(CH_2\cdot CH_2\cdot CH_2\cdot NH_2)_2,3HCl$, which yields a sparingly soluble platinochloride.

The mother liquor from the above diphthalyl compound, leaves on evaporation a yellow, resinous mass, which may be purified for analysis by recrystallisation from light petroleum. It then forms indistinct, yellow crystals melting at 87—89°, which from their composition and mode of preparation must consist of *γ-anilidopropylphthalimide*, $C_8H_4O_2:N\cdot CH_2\cdot CH_2\cdot CH_2\cdot NHPh$. Like the foregoing compound, this is converted by treatment with fuming hydrochloric acid into the *hydrochloride* of the corresponding trimethylenephenyldiamine, $NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NHPh,2HCl$, which crystallises in small, almost white needles. The *picrate*, $C_9H_{14}N_2,2C_6H_3N_3O_7$, crystallises from 60 per cent. alcohol in greenish, feathery needles, which decompose

at 195°. The free *trimethylenephenyldiamine*, $NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NHPh$ is prepared by decomposing a concentrated aqueous solution of the hydrochloride with solid potash. It is a colourless, strongly refractive oil, readily soluble in water, alcohol, and ether, having a strong alkaline reaction and characteristic amine smell, and boiling at 277°. It absorbs carbonic anhydride from the air, forming a liquid carbonate. This base has also been prepared in a different manner by Balbiano (Abstr., 1889, 1215). In agreement with the latter, the author finds that the amido-compound reacts with carbon bisulphide in a different manner to ethylenediamine, a *dithiocarbamate* of the constitution $NH \cdot Ph \cdot C_3H_6 \cdot NH \cdot CS \cdot SH, NHPh \cdot C_3H_6 \cdot NH_2$, being formed. It crystallises in small, white plates and decomposes on boiling with water into hydrogen sulphide, trimethylenephenyldiamine, and *trimethylenephenylthiocarbamide*, $CS<\substack{NH-\\N \cdot Ph}>C_3H_6$, the latter forming white prisms melting at 215°.

Trimethylenephenyldiamine is readily acted on by phenylthiocarbimide with formation of trimethylene, triphenyldithiocarbamide, $NHPh \cdot CS \cdot NH \cdot C_3H_6 \cdot NPh \cdot CS \cdot NHPh$, which crystallises from alcohol in slender needles melting at 145°.

Trimethylenephenylcarbamide cannot be prepared in a similar manner to the corresponding trimethylenecarbamide by the action of ethyl carbonate on trimethylenephenyldiamine (compare Fischer and Koch, Abstr., 1886, 527). If, however, the monohydrochloride of the latter be treated with potassium cyanate at 100°, it is converted into *anilidopropylcarbamide*, $NH \cdot Ph \cdot C_3H_6 \cdot NH \cdot CO \cdot NH_2$. This crystallises in rose-coloured aggregates of needles which melt at 96—98°, and at 120° give off ammonia with formation of *trimethylenephenylcarbamide*, $CO<\substack{NPh\\NH-}>C_3H_6$. This crystallises from alcohol in pale yellow needles sparingly soluble in water, and melts at 213—215°.

H. G. C.

Derivatives of Paracyanobenzyl Chloride. By H. K. GÜNTHER (*Ber.*, **23**, 1058—1062).—*Paracyanobenzylphthalimide*,

$$C_8H_4O_2 \vdots N \cdot CH_2 \cdot C_6H_4 \cdot CN,$$

is formed when paracyanobenzyl chloride is heated with potassium phthalimide at 130°. It crystallises from boiling glacial acetic acid in yellowish-brown plates, $a : b : c = 0 \cdot 7212 : 1 : 0 \cdot 5218$, melts at 183—184°, and is almost insoluble in water, ether, alcohol, and light petroleum, but readily soluble in acetone, chloroform, and hot glacial acetic acid.

Paracarboxybenzylphthalamic acid,

$$COOH \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot C_6H_4 \cdot COOH,$$

is obtained when the preceding compound is warmed with soda, and the sodium salt thus produced decomposed with hydrochloric acid. It separates from alcohol in microscopic needles, melts at 255°, and is only sparingly soluble in most ordinary solvents. The *silver* salt, $C_{16}H_{12}O_5NAg_2$, crystallises in prisms.

Benzylamineparacarboxylic acid, $NH_2 \cdot CH_2 \cdot C_6H_4 \cdot COOH$, can be pre-

pared by heating the preceding compound with concentrated hydrochloric acid at 200° for three hours; the product is treated with cold water, the filtered solution evaporated to dryness, the residue dissolved in a little warm water, and the solution mixed with sodium acetate; on rubbing, the acid gradually separates in crystals. It crystallises from water and glacial acetic acid in yellow scales, and is insoluble in ether, alcohol, benzene, acetone, and light petroleum. The *hydrochloride* crystallises in long needles, $a : b : c = 0·5742 : 1 : 0·9630$, and is soluble in water, alcohol, light petroleum, and chloroform, but insoluble in ether, glacial acetic acid, and benzene. The *platinochloride* $(C_8H_9O_2N)_2,H_2PtCl_6$ is amorphous. The *aurochloride* crystallises in well-defined prisms.

An acid of the composition $C_{16}H_{14}O_5$ is formed when paracyanobenzyl chloride is boiled with potash, and the resulting sodium salt decomposed with hydrochloric acid; it separates from hot acetic acid in ill-defined, colourless crystals, and is insoluble in ether, acetone, chloroform, and benzene, but readily soluble in ammonia and alkalis. The *silver* salt has the composition $C_{16}H_{12}Ag_2O_5$. The constitution of the acid is probably expressed by the formula $O(CH_2·C_6H_4·COOH)_2$.

F. S. K.

Etard's Reaction. By W. v. MILLER and G. ROHDE (*Ber.*, **23**, 1070—1079).—When propylbenzene is treated with chromyl chloride, benzaldehyde, benzyl methyl ketone, and other compounds are formed, but not a trace of hydrocinnamaldehyde is produced, as stated by Etard (Abstr., 1881, 581).

When cymene is treated with chromyl chloride, it yields about equal quantities of an aldehyde identical with the compound described as paramethylhydrocinnamaldehyde by Richter and Schüchner (Abstr., 1884, 1342), and a compound which seems to be paratolylethyl ketone. The aldehyde obtained in this way is not identical with paramethylhydrocinnamaldehyde (compare next abstract), and on oxidation with silver oxide it is converted into an acid which melts at 40—41°; paramethylhydrocinnamic acid melts at 116° (compare Kröber, this vol., p. 969). The aldehyde obtained from cymene has probably the constitution $C_6H_4Me·CHMe·CHO$, and the acid (m. p. 40—41°) is probably paramethylhydratropic acid.

Ethylbenzene and chromyl chloride yield acetophenone, together with an oil which combines with sodium hydrogen sulphite, and probably consists of phenylacetaldehyde and benzaldehyde.

The above experiments show that Etard's reaction takes a course different to that which it is usually supposed to take; whilst the methylbenzenes yield with chromyl chloride the corresponding aldehydes, the hydrocarbons with longer side chains give a ketone as a rule, and only in some cases the corresponding aldehyde.

Stilbene is formed when a mixture of benzyl methyl ketone and benzaldehyde is shaken with hot concentrated (3 : 1) sulphuric acid; when a mixture of benzyl methyl ketone and metachlorobenzaldehyde is treated in like manner, a crystalline compound melting at 73—74°, probably metachlorostilbene, is produced. Deoxybenzoïn and benzyl methyl ketone condense together forming stilbene and benzoic acid.

F. S. K.

Hydrocinnamaldehydes. By W. v. MILLER and G. ROHDE (*Ber.*, **23**, 1079—1082).—*Hydrocinnamaldehyde*, $C_6H_5·CH_2·CH_2·CHO$, prepared by distilling a mixture of calcium hydrocinnamate and calcium formate, is an oil.

α-Methylhydrocinnamaldehyde, $C_6H_5·CH_2·CHMe·COH$, prepared from methylhydrocinnamic acid in like manner, boils at 226—227° (corr.); the hydrazone and the anilide are oils.

Metachlorohydrocinnamaldehyde, C_9H_9ClO, boils at about 240°.

Paramethylhydrocinnamaldehyde, $C_6H_4Me·CH_2·CH_2·CHO$, is an oil.

The compounds described above have a characteristic odour of jessamine, undergo oxidation on long exposure to the air, and have the generic properties of aldehydes; when treated with concentrated or moderately concentrated sulphuric acid, they yield solutions which, when seen by transmitted light, have a more or less intense rose- or carmine-red coloration. F. S. K.

Aromatic Alkyl Ketones; their Oxidation by Potassium Permanganate. By A. CLAUS (*J. pr. Chem.*, [2], **41**, 483—514; compare this vol., p. 769).—*Metaxylyl methyl carbinol*,

$$[C_6H_3Me_2·CHMe·OH = 2:4:1],$$

is produced when metaxylyl methyl ketone (Abstr., 1886, 463) is reduced by sodium amalgam (compare the behaviour of paratolyl methyl ketone, this vol., p. 769); it is a pale-yellow oil, becoming brown in the light in presence of air; it boils above 300°.

Metaxylyl methyl ketone *phenylhydrazide* forms lustrous needles melting at 115° (uncorr.), and is insoluble in cold water and ether.

Orthoparadimethylmandelic acid,

$$C_6H_3Me_2·CH(OH)·COOH\ [= 2:4:1],$$

is obtained when metaxylylglyoxylic acid (Abstr., 1886, 463) is reduced by sodium amalgam; it crystallises from hot water in aggregates of needles, melts at 119° (uncorr.), sublimes, and is easily soluble in alcohol and ether, but not in cold water. It gives a cherry-red colour when warmed with strong sulphuric acid, a reaction which is shared by its salts. When the glyoxylic acid is reduced by hydriodic acid, metaxylylacetic acid, $C_6H_3Me_2·CH_2·COOH$ [4:2:1], is obtained as well as the above; it crystallises in colourless needles or leaflets which melt at 102° (uncorr.), sublime, and are soluble in the usual solvents, except cold water. The melted acid distils about 265° (uncorr.). Its *potassium*, *barium*, and *silver* salts (each with 1 mol. H_2O), its *calcium salt* (with $4\frac{1}{2}$ mols. H_2O), and its *amide* (m. p. 183°, uncorr.) are described.

Dinitrosometaxylylglyoxylic acid, $C_6HMe_2(NO)_2·CO·COOH$, obtained by acting on the glyoxylic acid (1 part) for a short time (two minutes) with fuming nitric acid (4—5 parts), forms colourless crystals which melt at 177° (uncorr.), and sublime with decomposition; it is soluble in the usual solvents, except water, and gives a red colour with phenol and sulphuric acid. Its *potassium* and *barium* salts (each with $1\frac{1}{2}$ mol. H_2O) are described. When it is oxidised with potassium chromate (0·254 part) and sulphuric

acid, it yields *dinitrosometaxylenecarboxylic acid*, $C_6HMe_2(NO)_2\cdot COOH$, which melts at 166°. When the dinitrosoglyoxylic acid is acted on by fuming nitric acid, *nitronitrosometaxylenecarboxylic acid*,

$$NO\cdot C_6HMe_2(NO_2)\cdot COOH,$$

is obtained; this crystallises in needles which melt at 256° (uncorr.), and dissolve freely in hot water, sparingly in chloroform and glacial acetic acid, but not in carbon bisulphide and benzene.

Dinitrometaxylylglyoxylic acid,

$$C_6HMe_2(NO_2)_2\cdot CO\cdot COOH\ [=2:4:3:5:1],$$

is obtained by treating xylylglyoxylic acid with nitric and sulphuric acids in the cold and pouring the mixture into water; it forms colourless needles melting at 198° (uncorr.); its *barium salt* (with 2 mols. H_2O) is described.

By nitrating metaxylyl methyl ketone (10 grams) with nitric acid of sp. gr. 1·4 (100 grams) at 65°, a nitroso-derivative,

$$(C_8H_9\cdot CO\cdot C{:}N\cdot OH)_x,$$

melting at 107—108°, was obtained: this has been described by Holleman (Abstr., 1888, 275; 1889, 49). When it is oxidised by potassium permanganate, it yields orthoparadimethylbenzoic acid (m. p. 126°), and when it is reduced by zinc and acetic acid, dimetaxylyl ethylene diketone (Abstr., 1887, 827) is obtained.

When nitric acid, of sp. gr. 1·52, is used, and the temperature kept below 30°, two mononitro-metaxylyl methyl ketones are obtained, the one (m. p. 72°) more soluble in alcohol than the other (m. p. 67°); a third product was obtained but not investigated.

5-*Nitrometaxylyl methyl ketone* forms colourless needles which melt at 67° (uncorr.) and are insoluble in dilute alcohol. When it is oxidised with dilute nitric acid, or potassium permanganate, nitrodimethylbenzoic acid (m. p. 195°) is formed; the *amido*-derivative of this acid melts at 175°. When the potassium permanganate is used in dilute aqueous solution and in sufficient quantity to supply only three atoms of oxygen, 5-*nitro*-2 : 4-*dimethylphenylglyoxylic acid* is formed; it is an oil which crystallises after a time and melts at 40° (?); its *barium salt* (with 6 mols. H_2O), *calcium salt* (with $4\frac{1}{2}$ mols. H_2O), and *silver salt* are described. 5-*Amidometaxylyl methyl ketone* crystallises in small needles which quickly become coloured and melt at 88° (uncorr.); its *hydrochoride* and *platinochloride* are described.

3-*Nitrometaxylyl methyl ketone* crystallises from glacial acetic acid in columns or prisms which melt at 72°; it is unstable and gradually becomes converted into an oily substance, referred to above as the third product of the action of nitric acid on metaxylyl methyl ketone. When oxidised with four atoms of oxygen, it yields 3-*nitro*-2 : 4-*dimethylbenzoic acid*; this acid forms colourless needles or columns which melt at 135° (uncorr.), and are freely soluble, except in cold water; its *barium salt* was obtained.

When metaxylyl methyl ketone (1 part) is added by degrees to a mixture of nitric acid of sp. gr. 1·52 (3 parts) and sulphuric acid (6 parts), cooled to −10° or −15°, two products are obtained, a dinitro- and a dinitronitroso-ketone, the latter being more abundant

at higher temperatures; the dinitroketone is soluble in ether, which therefore serves to separate them.

3 : 5-*Dinitrometaxylyl methyl ketone* crystallises in yellow needles which melt at 96° (uncorr.) and explode at the boiling point; it is soluble in the usual solvents. By oxidation it yields 3 : 5-*dinitro-2 : 4-dimethylbenzoic acid*, which forms small, lustrous crystals melting at 199—200° (uncorr.) and subliming in silky needles; it is freely soluble, except in cold water; its *potassium*, *barium* (with $1\frac{1}{2}$ mols. H_2O), *calcium*, and *silver* salts were obtained; they are explosive when dry.

3 : 5-*Dinitrometaxylyl nitrosomethyl ketone* crystallises from nitrobenzene, or acetone, in lustrous, microscopic leaflets melting at 209° (uncorr.), and exploding when heated on platinum foil.

Mesityl methyl ketone, $C_6H_2Me_3{\cdot}COMe$, is a colourless liquid of peculiar odour; it boils at 235° (uncorr.), and is specifically lighter than water. When it is oxidised by potassium permanganate, mesitylglyoxylic acid and trimethylbenzoic acid are obtained; they are separated by water at 30°, in which the latter is fairly soluble, but the former not.

Mesitylglyoxylic acid forms large, yellowish, columnar crystals melting at 118° (uncorr.), and soluble except in water. The *barium salt* (with $2\frac{1}{2}$ mols. H_2O) and the *silver salt* are described.

2 : 4 : 6-*Trimethylbenzoic acid* forms crystals which melt at 155° (uncorr.); it is volatile with steam, smells of honey, sublimes, and is freely soluble in the usual solvents; it is identical with Jacobsen's β-isodurylic acid (m. p. 151°; Abstr., 1883, 53). The *barium salt* (with 2 mols. H_2O) and the *silver salt* are described. Further oxidation by potassium permanganate produces only one dibasic acid, namely, 2 : 6-*dimethylterephthalic acid;* this acid crystallises in small, white needles which melt at 206° (uncorr.) and are easily soluble; the *barium salt* (with 3 mols. H_2O) is described.

2 : 4 : 6-*Trimethylphenylacetamide*, $C_6H_2Me_3{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, is obtained by the action of ammonium sulphide on mesityl methyl ketone in small, colourless crystals which melt at 208° (uncorr.) and sublime; it is soluble except in cold water. The corresponding *acid* forms a white, crystalline powder which melts at 164° (uncorr.) and sublimes in small, colourless, slender needles; it is soluble except in cold water; the *barium salt* (with 3 mols. H_2O) was obtained.

Pseudocumyl methyl ketone [$Me_3 = 2 : 4 : 5$] is a colourless, strongly refracting liquid which boils at 246—247° (uncorr.); it solidifies at 0° to transparent prisms which melt at 10°; it dissolves in the usual solvents. When oxidised, it yields 2 : 4 : 5-*trimethylphenylglyoxylic acid*, which crystallises in slender, white needles melting at 75° (uncorr.), and is soluble in most solvents; its *potassium* (with 1 mol. H_2O), *sodium* (with $1\frac{1}{2}$ mols. H_2O), *barium* (with 4 mols. H_2O), *calcium* (with 3 mols. H_2O), *silver*, and *lead* salts were obtained. When this glyoxylic acid is treated with ammonium sulphide, 2 : 4 : 5-*trimethylphenylacetamide* is formed; it crystallises in lustrous leaflets which melt at 174°. The corresponding *acid* forms needles which melt at 118° (uncorr.) and sublime; the *barium* salt crystallises with 2 mols. H_2O. By oxidation, the glyoxylic acid becomes 2 : 4 : 5 *trimethylbenzoic*

acid (m. p. 150°), identical with Jannasch's durylic acid (*Zeits. f. Chem.*, **6**, 449), some 2 : 5-*dimethylterephthalic acid*, identical with Jannasch's cumidic acid (*loc. cit.*; Abstr., 1883, 334), being formed at the same time. A. G. B.

Dipyrogallopropionic Acid. By C. Böttinger (*Ber.*, **23**, 1093).—The compound described by the author as dipyrogallopropionic acid (Abstr., 1884, 318) has, like Doebner and Förster's pyrogallolbenzeïn (this vol., p. 899), the property of dissolving in alkalis with a beautiful blue coloration.

The so-called dipyrogallopropionic acid can be converted into a tetracetyl-derivative; when its red solution is boiled with zinc-dust and glacial acetic acid, it becomes colourless, but on the addition of soda the reduction product absorbs oxygen and the solution turns blue. The colourless reduction product is probably the true dipyrogallopropionic acid, of which the red compound is an oxidation product. F. S. K.

Tetrabromodinitrobenzene. By C. L. Jackson and W. D. Bancroft (*Amer. Chem. J.*, **12**, 289—307; compare Abstr., 1888, 821 and 1276; 1889, 696).—Tetrabromodinitrobenzene (m. p. 228°) is not acted on by alcoholic ammonia in open vessels, but if the mixture is heated in sealed tubes at 100°, it is converted into a substance (probably *bromotriamidodinitrobenzene*) which is insoluble in any ordinary solvent, and does not melt at 285°.

Bromodinitrotrianilidobenzene, $C_6Br(NO_2)_2(NHPh)_3$ is prepared by heating at 100°, a mixture of tetrabromodinitrobenzene (1 mol.) and aniline (6 mols.). It is insoluble in water and light petroleum; crystallises from alcohol, acetic acid, benzene, and chloroform in microscopic prisms; and melts at 175—176°. The compound has no basic properties.

Ethyl dibromodinitrophenylmalonate, $C_6HBr_2(NO_2)_2\cdot CH(COOEt)_2$, is obtained by dissolving tetrabromodinitrobenzene in benzene, and mixing the solution with ethyl sodiomalonate; the red-coloured mass formed is poured into water and the benzene separated; on adding sulphuric acid to the aqueous solution, the new compound separates out, and on crystallisation from alcohol forms colourless needles which melt at 89°. It is insoluble in water and in light petroleum, but is readily dissolved by all other common solvents, has well-marked acid properties, forms soluble salts with the alkalis, and gives various-coloured, amorphous precipitates when solutions of the heavy metals are added to aqueous solutions of its ammonium salt.

Ethyl bromanilidodinitrophenylmalonate,

$$NHPh\cdot C_6HBr(NO_2)_2\cdot CH(COOEt)_2,$$

is readily prepared by adding aniline (2 mols.) to ethyl dibromodinitrophenylmalonate (1 mol.). It crystallises from hot alcohol in slender, bright-red prisms; melts at 127°; readily dissolves in most solvents; has only feeble acid properties, but gives yellow precipitates with solutions of the heavy metals.

Bromamido-oxindole, $C_8NH_5OBr\cdot NH_2$, is obtained by the reduction

of ethyl dibromodinitrophenylmalonate with tin and hydrochloric acid. On precipitation from a solution of its chloride, it forms colourless, microscopic needles which melt, with considerable charring, at about 212°. It is soluble in hot water and in hot alcohol, insoluble in ether and chloroform, and, in some respects, behaves as a phenol. The chloride, $C_8H_7ON_2,HCl + H_2O$, crystallises from water in needles or prisms, and does not melt within the range of the mercurial thermometer.

In preparing tetrabromodinitrobenzene for these experiments, the previously undescribed pentabromonitrobenzene, melting at 248°, was obtained. G. T. M.

Compounds Prepared from Bromonitrobenzenes. By C. L. JACKSON (*Amer. Chem. J.*, **12**, 307—313; compare preceding abstract).—The author offers an explanation of the reactions between the bromonitrobenzenes prepared by him, on the one hand, and ethyl sodiomalonate on the other hand; reviews the relative ease with which the reactions takes place, and gives inferences drawn from experiments, by which the comparative acidity of the substituted ethyl malonates, ethyl acetoacetates and ketones, prepared by him, have been determined. G. T. M.

Tautomeric Compounds. By J. U. NEF (*Amer. Chem. J.*, **12**, 379—425; compare also Abstr., 1889, 509).—The first part of the paper is devoted to a discussion of the alleged cases of tautomerism in ethyl succinosuccinate and analogous compounds, and reasons are given for believing that the polymorphism in this group is due, not to a change of position of certain groups within the molecule, but to physical isomerism. It is further deemed probable that ethyl succinosuccinate and dihydroxyterephthalate never contain a ketone-group, but that the oxygen usually assumed to exist in this condition is present rather as hydroxyl.

The author then proceeds to give in detail the results of experiments made to test this alleged tautomerism, after first mentioning that he has prepared a derivative of ethyl acetoacetate containing two acid radicles, which has not before been done. Since ethyl acetoacetate greatly resembles ethyl succinosuccinate and dihydroxyterephthalate, it seemed probable that it, too, is not a ketonic compound, and if so it ought to form alkyl and acid ethereal salts, in which the substituting group (R) is bound to oxygen, OR·CMe:CH·COOEt, and these substances would be insoluble in alkalis. In reality, it is found that when ethyl sodacetacetate is treated with 1 mol. of benzoic chloride, a small quantity of a compound insoluble in alkalis is formed, but this was found to be ethyl dibenzoylacetoacetate, $COMe\cdot CBz_2\cdot COOEt$.

Ethyl dihydrodiamidopyromellitate, $C_6H_2(NH_2)_2(COOEt)_4$,

$$[(COOEt)_4 : (NH_2)_2 : H_2 = 1:3:4:6:2:5:1:4, = \Delta_{2,5}, \text{ or}$$

$1:3:4:6:2:5:3:6, = \Delta_{1,4}]$, is made by treating an alcoholic solution of ethyl diamidopyromellitate with zinc-dust and dilute sulphuric acid; it may also be obtained, though only in small quantity, by fusing

together ammonium acetate and ethyl paradiketohexamethylene-tetracarboxylate, into which latter substance it is itself converted when dissolved in concentrated sulphuric acid and treated with a little water. It dissolves in chloroform, and with difficulty in alcohol, from which it crystallises in colourless needles melting at 212°. When treated with 1 mol. of bromine, it loses its two hydrogen-atoms, and forms ethyl diamidopyromellitate. It also yields an acetyl-derivative melting at 132°.

Pyrazolone-derivative of dihydroxypyromellitic (quinoltetracarboxylic) acid, $C_6\left(\begin{matrix}NH\\CO\end{matrix}>NPh\right)_2(COOH)_2$, is best prepared by treating a hot aqueous solution of the acid with twice the theoretical amount of phenylhydrazine hydrochloride, and heating the mixture for three to five hours on the water-bath to complete the reaction. A hydrazide of the acid is probably first formed, and then loses two molecules of water, yielding the pyrazolone-derivative. This forms yellow crystals, which exhibit all the properties of a pyrazolone-derivative. When it is oxidised with fuming nitric acid, or when an alkaline solution of it (which is purple in colour) is oxidised with potassium ferrocyanide, or by simple exposure to the air, a very stable compound,

$$C_6\left(\begin{matrix}N-\\CO\end{matrix}>NPh\right)_2(COOH)_2,$$

is formed, which gives with alkalis a yellow solution exhibiting a green fluorescence. Two of the hydrogen-atoms in the pyrazolone-derivative are replaceable by metals. When it is heated with excess of benzoic chloride, the dibenzoyl-dipyrazolone anhydride,

$$O<\begin{matrix}CO\\CO\end{matrix}>C_6\left(\begin{matrix}NBz\\CO-\end{matrix}>NPh\right)_2,$$

is formed. This forms yellow crystals soluble in alcohol, melting at 140°, and volatilising without decomposition at a very high temperature. Both it and its solutions show a green fluorescence. After boiling with alcoholic soda, acids precipitate the free acid in yellow flakes, the benzoyl-groups not being eliminated.

Dihydroxypyromellitic acid, when heated with large excess of hydroxylamine hydrochloride, yields a hydroxamic acid, which is reconverted into the original acid when boiled with acids. When heated for 10 to 15 minutes at 300—350°, it forms *quinoltetracarboxylic anhydride*, $C_6(OH)_2\left(\begin{matrix}CO\\CO\end{matrix}>O\right)_2$, which is soluble in acetone and ethyl acetate, and crystallises from the latter in yellow prisms with red fluorescence. It volatilises without decomposition at 350°, and dissolves in water giving a red solution, which when left to itself, or heated, is transformed into the acid. Its alkaline salts are very deep red in colour.

Dihydroxypyromellitic acid yields bromanil, $C_6H_4Br_2$, when allowed to remain for 12 hours with excess of bromine and some water; quinone-tetracarboxylic acid, $C_6O_2(COOH)_4$, is probably first formed, and then its carboxyl-groups are replaced by bromine. It also yields chloranil when treated with potassium chlorate and hydrochloric acid,

but with iodine and hydriodic acid, it yields, not iodanil, but iodoform, and with nitric acid, nitranilic acid, $C_6O_2(NO_2)_2(OH)_2$, which is, however, doubtless derived from unstable nitranil first formed. Dihydrodihydroxypyromellitic acid could not be prepared either by saponification of its ethyl salt or by reduction of dihydroxypyromellitic acid, carboxyl-groups being always eliminated. These facts, together with those known regarding succinosuccinic acid, show how unstable hydroxybenzenecarboxylic acids are. But dihydroxyterephthalic acid, and still more so dihydroxypyromellitic acid are stable, and so one is led "to the inevitable conclusion that these are coloured benzene-derivatives, and that they can never exist as quinolcarboxylic acids."

The author now proceeds to prove that the substituted groups in derivatives of ethyl dihydroxypyromellitate and dihydrodihydroxypyromellitate (paradiketohexamethylenetetracarboxylate) are joined to oxygen, and not directly to carbon. This he does by converting ethyl dimethoxypyromellitate by heating with alcoholic soda into the sodium salt, this into the silver salt, and this finally into a substance melting at 134°, which is identified as methyl dimethoxypyromellitate. The intermediate product, $OMe\cdot C_6(ONa)(COOEt)_4$, obtained by the action of methyl iodide on ethyl disodoxypyromellitate, was also examined; it forms yellow plates with green fluorescence, soluble in alcohol. The best way of preparing sodium salts such as that mentioned above is to dissolve the substance (an ethyl salt, &c.) in chloroform, and add a solution in alcohol of the theoretical amount of sodium, diluted with chloroform; the sodium salt is precipitated in the gelatinous state, and is dried on a porous plate in the air, or at 100°.

Methyl dimethoxypyromellitate, $C_6(OMe)_2(COOMe)_4$ is formed by heating methyl disodoxypyromellitate, $C_6(ONa)_2(COOMe)_4$, with excess of methyl iodide in a sealed tube. It melts at 134°, and volatilises without decomposition. Its reactions show that it is a methoxy- and not a ketonic compound.

Methyl diacetoxypyromellitate, $C_6(OAc)_2(COOMe)_4$, is formed by the action of acetic chloride on the above-mentioned sodium salt. It melts at 147°, and volatilises without decomposition. Its reactions are those of an acetyl-derivative of a phenol.

Methyl dihydrodiacetoxypyromellitate, $C_6H_2(OAc_2)_2(COOMe)_4$, is formed by the action of zinc and hydrochloric acid on the preceding compound. It melts at 173°, and volatilises without decomposition. It is dimorphous. With bromine, it yields methyl dihydroxypyromellitate, $C_6(OH)_2(COOMe)_4$, melting at 207°; with nitric acid, it behaves exactly like methyl paradiketohexamethylenetetracarboxylate, yielding first ethyl dihydroxypyromellitate, and then ethyl quinonepyromellitate, melting at 208°. It may also be obtained from methyl disodioparadiketohexamethylenedicarboxylate and acetic chloride; hence methyl paradiketohexamethylenetetracarboxylate is not a ketonic but a methoxy-derivative.

Ethyl dibenzoyloxypyromellitate, $C_6(OBz)_2(COOEt)_4$, is formed by treating the corresponding disodium compound with benzoic chloride. It melts at 157°, and when reduced with zinc and hydrochloric acid,

yields *ethyl dihydrodibenzoyloxypyromellitate*, $C_6H_2(OBz)_2(COOEt)_4$, melting at 135°, and volatilising without decomposition. This substance is also formed when ethyl paradiketohexamethylenetetracarboxylate is treated with benzoic chloride. By bromine, it is reconverted into the pyromellitate, $C_6(OBz)_2(COOEt)_4$, melting at 157°; sulphuric acid decomposes it into benzoic acid and ethyl paradiketohexamethylenetetracarboxylate, melting at 143°.

The author now proceeds to prove that also in derivatives of ethyl dihydroxyterephthalate and succinosuccinate the substituted groups are united to oxygen.

Ethyl dimethoxyterephthalate, $C_6H_2(OMe)_2(COOEt)_2$ [$(OMe)_2 = 1:4$], was prepared from the corresponding sodium salt and methyl iodide. It forms colourless plates with a marked blue-violet fluorescence, melting at 101·5°, and volatilising without decomposition. Its entire behaviour shows that the methyl-groups are united to oxygen. When heated with dilute alcoholic soda, it yields *dimethoxyterephthalic acid*, $C_6H_2(OMe)_2(COOH)_2$, melting at 265°. It is not itself fluorescent, but in aqueous solution exhibits blue-violet fluorescence.

Ethyl dibenzyloxyterephthalate, $C_6H_2(O{\cdot}CH_2Ph)_2(COOEt)_2$, is formed by treating the corresponding disodium salt with benzyl chloride. It forms colourless needles exhibiting blue-violet fluorescence, melting at 96·5°, and volatilising without decomposition. It does not give the ordinary ketonic reactions. In the presence of alkalis, the benzyl groups are stable, but with acids, *ethyl dihydroxyterephthalate*, $C_6H_2(OH)_2(COOEt)_2$, melting at 133°, is formed, and bromine appears to replace some of the hydrogen of the benzyl-groups. When reduced with zinc and hydrochloric acid, it yields *ethyl α-dihydrodibenzyloxyterephthalate*, $C_6H_4(OCH_2Ph)_2(COOEt)_2$, which forms colourless crystals, with faint blue-violet fluorescence, melting at 169°, and volatilising without decomposition. It was impossible to remove any of the hydrogen-atoms. Three isomerides of this substance (six isomeric dihydrobenzene-derivatives are possible) are obtained by treating ethyl disodiosuccinosuccinate with benzyl chloride, namely, a β-variety melting at 148·5°, which is transformed by sulphuric acid into a polymeric second, ϖ-variety melting at 272°, and volatilising without decomposition, and a third, γ-variety melting at 140·5°, also volatile without decomposition. None of these compounds gives the ketonic reactions.

Ethyl diacetoxyterephthalate, $C_6H_2(OAc)_2(COOEt)_2$, prepared from ethyl disodoxyterephthalate and acetic chloride, melts at 154°, and is not acted on by bromine.

Ethyl diacetoxysuccinosuccinate, $C_6H_4(OAc)_2(COOEt)_2$, prepared from ethyl disodoxysuccinosuccinate, melts at 169°, and is converted by bromine into ethyl dihydroxyterephthalate. But these two substances are crystallographically absolutely identical. A similar isomorphism also occurs between *ethyl dibenzoyloxyterephthalate*, $C_6H_2(OBz)_2(COOEt)_2$, melting at 174°, and *ethyl α-dibenzoyloxysuccinosuccinate*, $C_6H_4(OBz)_2(COOEt)_2$, melting at 165°. The latter substance is formed by acting on ethyl disodoxysuccinosuccinate with benzoic chloride, and when treated with bromine yields ethyl dibenzoyloxyterephthalate. Ethyl dibenzoyloxyterephthalate is formed from the

disodoxyterephthalate and benzoic chloride; when reduced with zinc and aqueous hydrochloric acid, it yields three varieties of ethyl dihydrodibenzoyloxyterephthalate, $C_6H_4(OBz)_2(COOEt)_2$, an α-variety melting at 165°, identical with that obtained from the ethyl disodoxysuccinosuccinate, a β-variety melting at 138°, and a γ-variety melting at 102·5°; all three varieties volatilise without decomposition. If, however, alcoholic hydrochloric acid be used, the α-variety is obtained, together with two, possibly three, new isomerides.

Finally a few compounds are described to complete the work on durene (Abstr., 1887, 255). *Methyl dinitropyromellitate*, prepared from the silver salt and methyl iodide, forms long, flat, transparent needles, melting at 180·6°; when reduced, it yields *methyl diamidopyromellitate*, forming long, flat needles melting at 149·6°, and this on further reduction yields *methyl dihydrodihydroxypyromellitate* (*paradiketohexamethylenetetracarboxylate*) in heavy cubes with faint blue fluorescence, melting at 175°. This again, when treated with bromine, yields *methyl dihydroxypyromellitate*, which is a granular, yellow powder melting at 207°. *Methyl quinonepyromellitate*, $C_6O_2(COOMe)_4 + 2CH_3{\cdot}OH$, obtained by oxidation of the diamidopyromellitate with nitric acid, is colourless. At 150° it loses alcohol, becoming yellow; it then melts at 208°, and volatilises unchanged. C. F. B.

Hydrazobenzenedisulphonic Acid. By H. LIMPRICHT (*Ber.*, **23**, 1052—1057).—The compound obtained by the reduction of metanitrobenzenesulphonic acid, and described as hydrazobenzenesulphonic acid (Abstr., 1880, 805, 807, 808, 809), is, in reality, benzidinedisulphonic acid, as was suggested by Schultz. The true hydrazobenzenedisulphonic acid cannot be isolated, but it can be obtained in an impure condition as follows:—A solution of potassium metazobenzenedisulphonate is treated with a solution of basic lead acetate, the red, crystalline precipitate of the basic lead salt washed well with boiling water, then suspended in hot water, and treated with hydrogen sulphide; the colourless filtrate, on evaporation, yields a mixture of metamidobenzenesulphonic acid, benzidinesulphonic acid, and hydrazobenzenedisulphonic acid, from which the last-named compound can be obtained, mixed, however, with benzidinedisulphonic acid, by extracting with cold water. It forms colourless crystals, is readily soluble in water, and has powerful reducing properties; when treated with mineral acids, it is converted into benzidinedisulphonic acid, and when its alkaline solution is evaporated, it is converted into azobenzenedisulphonic acid. The *barium* salt, $C_{12}H_{10}S_2N_2O_6Ba$, is a colourless, or yellowish, crystalline compound, only sparingly soluble in hot water, and insoluble in alcohol; it seems to crystallise with 2 mols. of water. The *potassium* salt, $C_{12}H_{10}S_2N_2O_6K_2$, is crystalline.

F. S. K.

Decomposition of Sulphones. By E. STUFFER (*Ber.*, **23**, 1408—1414).—It is well known that certain sulphones are quite stable towards alkalis, whilst others are readily hydrolysed The author has studied the action of alkalis on a number of different sulphones, for the purpose of discovering the connection between their constitution and decomposibility. Compounds of the formulæ

$CH_2(SO_2R)_2$ and $R'\cdot CH(SO_2R)_2$ are unacted on by alkalis; an increase in the length of the carbon chain (R) linked to the SO_2-group, does not influence this result. Trimethylenediethylsulphone and trimethylenediphenylsulphone are also unaffected by alkalis. On the other hand, the isomeric *propylenediphenylsulphone*,

$$SO_2Ph\cdot CHMe\cdot CH_2\cdot SO_2Ph,$$

which forms colourless crystals, and melts at 113—114°, reacts with alkalis with elimination of one phenylsulphone-group, in this respect resembling ethylenediphenylsulphone.

The author has also prepared *diphenylsulphonebromopropane*, $C_3H_5Br(SO_2Ph)_2$, and *triphenylsulphonepropane*, $C_3H_5(SO_2Ph)_3$. The former compound is obtained by warming a mixture of allyl bromide and sodium phenylmercaptide; on pouring into water, an oily liquid separates, which is purified by treating with potassium permanganate and dilute sulphuric acid; it crystallises from alcohol in colourless needles melting at 160°, and is easily hydrolysed. Triphenylsulphonepropane is prepared by boiling allyl tribromide with an alcoholic solution of sodium benzenesulphonate. The compound crystallises from dilute alcohol in colourless needles melting at 226°, and is readily hydrolysed on warming with alkalis. J. B. T.

Oxidation of Phenyl Trithioformate. By E. LAVES (*Ber.*, **23**, 1414—1417).—Phenyl trithioformate is dissolved in benzene and treated with slight excess of potassium permanganate solution and dilute sulphuric acid. The filtrate from the manganese precipitate contains benzenesulphonic acid. The manganese precipitate is dried and extracted with boiling alcohol; on cooling, *methyldiphenylsulphone phenyl sulphide*, $SPh\cdot CH\cdot(SO_2Ph)_2$, separates in lustrous, silky needles melting at 174—175°. The compound is sparingly soluble in cold water; it has acid properties, and dissolves in sodium hydroxide solution in the cold, and in sodium carbonate solution on heating; from each of these it is reprecipitated unchanged by acids. On oxidation, the corresponding trisulphone is formed melting at 215°.

Ethenyldiphenylsulphone phenyl sulphide, $SPh\cdot CMe(SO_2Ph)_2$, is obtained by dissolving the above compound in dilute alcoholic sodium hydroxide, and heating the solution, together with methyl iodide, in a sealed tube; it crystallises from chloroform, and melts at 194° with previous softening. Benzenesulphonic acid is obtained as sole product by the oxidation of phenyl trithioformate with alkaline potassium permanganate solution.

The above results are in apparent contradiction to the observations of Gabriel (compare Abstr., 1877, 311), who obtained phenyl disulphide by the oxidation of phenyl trithioformate. J. B. T.

Acetyl-derivatives of Indole. By C. ZATTI and A. FERRATINI (*Ber.*, **23**, 1359—1361).—1'-*Acetylindole*, C_8NH_6Ac, corresponding with 1-acetylpyrroline, may be readily prepared by acting on indole with acetic anhydride in the usual manner, evaporating the excess of the latter in a vacuum, and then distilling the residue with steam. The yellowish, oily liquid obtained is purified by redistillation in a

current of steam, and then fractionated under reduced pressure. It boils at 152—153° under 14 mm. pressure, with slight decomposition, and has an odour resembling that of the known acetyl-derivatives of pyrroline and indole. It is readily decomposed by alkalis into indole and acetic acid.

The acetyl compounds remaining after the first treatment with steam consist of the two known acetyl-derivatives of indole in almost equal proportions. The original product, on treatment with anhydrous reagents, yields almost solely the 1′ : 3′-diacetylindole, and it would therefore appear that the latter has been partially converted into 3′-acetylindole by the action of the water. Experiment has shown that 1′ : 3′-diacetylindole is in reality thus decomposed on long-continued boiling with water.

3′-Acetylindole undergoes condensation on treatment with benzaldehyde forming *3′-cinnamylindole*, $C_{17}H_{13}NO$, which crystallises from alcohol in small, yellow, lustrous plates melting at 229—231°, and corresponding exactly with the compound obtained in a similar manner from 1′-acetylpyrroline. Unsuccessful attempts were made to convert this by oxidation into an acid corresponding with pyrrylglyoxylic acid. H. G. C.

Benzilorthocarboxylic Acid. By C. GRAEBE (*Ber.*, **23**, 1344—1349).—It was observed by Juillard and Graebe (Abstr., 1888, 1095) that benzilorthocarboxylic acid exists in two modifications, one of which is yellow and the other white. Further investigation has confirmed this result, and has shown that the two compounds differ not only in their colour, but also in melting point and in solubility in concentrated alcohol, 50 per cent. alcohol, and chloroform. In their chemical relationships, however, no difference has yet been found.

In the preparation of benzilorthocarboxylic acid by the oxidation of desoxybenzoïncarboxylic acid, a mixture of both modifications is formed, and, on recrystallisation from water or dilute alcohol, a mixture of white and yellow crystals is also usually obtained. By very slow crystallisation from chloroform, and at a low temperature, both the mixture and the yellow modification are completely converted into the white compound. The yellow modification is best prepared by heating the mixture by itself to 140—150°, or with benzene to 160—180°, in a sealed tube.

The molecular weight, as found by Raoult's method, was the same for both acids. Both dissolve in solutions of alkalis and alkaline carbonates, forming a yellow solution from which acids precipitate the unaltered substances. By the action of concentrated alkalis, both yield the same benzhydroldicarboxylic acid. They also yield the same ethyl salt, melting at 71°, and the same monoxime,

$$COPh{\cdot}C(NOH){\cdot}C_6H_4{\cdot}COOH,$$

which is colourless, melts at 166°, does not lose water at 100°, and may be converted into the dioxime, which at once loses water, forming the anhydride. The carboxyl-group is not altered in the formation of the anhydride. The monoxime also readily yields a hydr-

azone, and phenylhydrazine also acts readily on the yellow and white modifications forming the same hydrazone.

The difference in colour of the two compounds is most readily explained by assuming a structure of the two compounds similar to that given by Victor Meyer for benzile and isobenzile, namely, $Ph{\cdot}CO{\cdot}CO{\cdot}Ph$ and $O<\begin{array}{c}CPh\\ | \\ CPh\end{array}>O$. The extreme readiness with which one modification passes into the other is against this view, and the author thinks that the isomerism is best explained in a similar manner to that of the benziledioximes, as given by V. Meyer and Auwers. According to this hypothesis, the carboxyl exercises such an influence on the benzile molecule that two configurations are possible, the one of which is formed chiefly at a low and the other at a high temperature. If the carboxyl-group be converted into the group COOEt, its influence is lessened, and only that modification corresponding with benzile is formed, and the addition of an oximido-group appears to produce a like effect. If two carboxyl-groups are introduced into benzile, as in diphthalic acid, their influence becomes so strong that only the colourless modification exists, whereas if the acid be converted into an ethereal salt, their influence is so much weakened that a white and yellow modification are again obtained, as has been shown experimentally for the methyl salts.

If this hypothesis is correct, it then becomes necessary to ascertain to which of the possible configurations of benzile, namely, $\begin{array}{l}Ph{\cdot}C : O\\ \quad | \\ O : C{\cdot}Ph\end{array}$ and $\begin{array}{l}O{:}C{\cdot}Ph\\ \quad | \\ O{:}C{\cdot}Ph\end{array}$, these modifications correspond. On this question the formation of anhydrides may throw some light. Thus the two oximes of desoxybenzoïncarboxylic acid both yield anhydrides of the formulæ $\begin{array}{l}Ph{\cdot}C{\cdot}CH_2{\cdot}C_6H_4\\ \;\;\| \qquad\quad | \\ \;\;N-O-CO\end{array}$ and $\begin{array}{l}Ph{\cdot}CH_2{\cdot}C-C_6H_4\\ \qquad\quad \| \quad | \\ \qquad\quad N{\cdot}O{\cdot}CO\end{array}$, whilst the monoxime of benzilemonocarboxylic acid does not yield an anhydride. In the first case, therefore, either free rotation is possible or the carboxyl-group is originally in such a position that separation of water can readily take place, whilst in the case of benzilemonocarboxylic acid monoxime free rotation cannot take place, and the carboxyl-group is not in a position which allows of the elimination of water. Diphthalic acid dioxime also readily yields an anhydride, which, according to Juillard and Graebe (*loc. cit.*), is a dilactone, the formation of which must be rendered possible by the relative position of the carboxyl- and carbonyl-groups.

The formation of anhydrides, which should always be possible if free rotation can take place, appears to be most readily understood on Victor Meyer's hypothesis. A large amount of experimental work is, however, necessary before the question can be regarded as settled, and the author is therefore continuing his investigation with a view to this end.

H. G. C.

Azo-derivatives of Phenyl-β-naphthylamine. By T. Zincke (*Ber.*, 23, 1315—1325).—According to Zincke and Campbell (this vol., p. 787), the azimido-compounds contain the group $—N{:}N{\cdot}N{\cdot}R$, and

not, as usually supposed, the group $\begin{matrix}N\\|\\N\end{matrix}\!\!>N\cdot R$. The formula given by Zincke and Lawson for the ammonium base obtained by the oxidation of benzeneazophenyl-β-naphthylamine (Abstr., 1887, 731) therefore requires alteration. If this compound is an azammonium compound corresponding with those obtained by the action of alkyl iodides on azimido-compounds, its constitution would be represented by the formula I, in favour of which is the fact that the oxidation compound resembles the latter substances in having a bitter taste, and in the fact that the free base readily undergoes decomposition.

$$C_{10}H_6\!<\!\begin{matrix}\text{———}N\\ NPh_2(OH)\end{matrix}\!\gg\!N \qquad C_{10}H_6\!<\!\begin{matrix}NPh(OH)\\|\\N\text{———}\end{matrix}\!>\!NPh$$

I. II.

$$C_{10}H_6\!<\!\begin{matrix}N\text{—}\\|\\NPh\end{matrix}\!\gg\!NPh\cdot OH.$$

III.

Experiments made to obtain evidence of a direct connection between these compounds have, however, only given negative results. Thus it was not found possible to convert the azimido-compound

$$C_{10}H_6\!<\!\begin{matrix}\text{—}N\\ NPh\end{matrix}\!\gg\!N$$

into the chloride $C_{10}H_6\!<\!\begin{matrix}\text{——}N\\ NPh_2Cl\end{matrix}\!\gg\!N$, and compare this with the chloride obtained from the oxidation compound. An unsuccessful attempt was also made to convert the azammonium compound $C_{10}H_6\!<\!\begin{matrix}\text{———}N\\ NMePhCl\end{matrix}\!\gg\!N$, by oxidation, into the compound

$$NHMe\cdot C_{10}H_6\cdot N_2Ph.$$

It was therefore necessary to consider the other possible formulæ, which are given above in II and III, and whose formation from the azo-compound may be readily understood. They explain also the fact that the ammonium base is readily reconverted into the azo-compound, either by heating its aqueous solution or by the action of reducing agents. In the first case, the oxygen set free acts on a portion of the original substance, forming a new base, which has the formula $C_{22}H_{15}N_3O$. More energetic reduction converts the azo-compound into phenyl-β-naphthylamine and aniline. This reaction, although readily explained by formulæ II and III, is not in favour of formula I, as, if that were correct, the phenyl must change its position in the reaction. On the other hand, it is not easy to understand why the linkage of the nitrogen-atoms assumed in II and III does not remain unaltered when the hydrogen takes the place of the hydroxyl-group.

Experiments made to ascertain whether this oxidation-product and the azammonium compounds were acted on in the same way were without success, but the investigations of Matthes (see next abstract), on the oxidation of isomeric azo-compounds, have given

more favourable results. If the formula I be correct, the isomeric azo-compounds $C_7H_7 \cdot NH \cdot C_{10}H_6 \cdot N_2Ph$ and $NHPh \cdot C_{10}H_6 \cdot N_2 \cdot C_7H_7$ would yield, on oxidation, one and the same base; whereas, if the second or third formula is correct, different bases would be obtained. The results given below show that two different bases are formed. This is, therefore, in favour of formula II or III, but cannot be regarded as a proof, as geometrical isomerides of the first formula might possibly exist. Further experiments are therefore necessary for the full explanation of these reactions.

The above ammonium base is poisonous, acting chiefly on the brain.

H. G. C.

Azo-derivatives of Secondary β-Naphthylamines. By P. MATTHES (*Ber.*, **23**, 1325—1334).—The compounds described below were prepared according to the method given by Zincke and Lawson (Abstr., 1887, 730); in consequence, however, of the tendency of many of the compounds to form azines, an excess of acid and too high a temperature must be avoided. The oxidation was carried out sometimes with chromic acid, sometimes with potassium dichromate, and the chromates formed converted into the hydrochlorides by the action of alcohol and hydrochloric acid.

Paratolueneazo-β-naphthylphenylamine, $NHPh \cdot C_{10}H_6 \cdot N_2 \cdot C_7H_7$, is obtained from β-naphthylphenylamine, and paradiazotoluene chloride, and crystallises from hot alcohol or acetic acid in deep-red needles having a fine metallic lustre, and melting at 120°. On oxidation, it forms an ammonium base, $C_{23}H_{17}N_3$, which is best isolated as the nitrate, the hydrochloride and sulphate being very soluble. The *nitrate* is sparingly soluble in water and cold alcohol, more readily in hot alcohol, and forms slender, slightly-yellow needles melting at 284—285°, and reddening at 140°. The *picrate*,

$$C_{23}H_{17}N_3,C_6H_2(NO_2)_3 \cdot OH,$$

forms slender, yellow needles melting at 238—239°; the *platinochloride*, $(C_{23}H_{17}N_3)_2,H_2PtCl_6$, a granular, yellow precipitate; the *mercurochloride*, $C_{23}H_{17}N_3,HHgCl_3$, a white, crystalline precipitate; and the *stannochloride*, $C_{23}H_{17}N_3,HSnCl_3$, small, yellow needles which become brown at 145° and melt at 175—176°.

Benzeneazo-β-naphthyltolylamine, $C_7H_7 \cdot NH \cdot C_{10}H_6 \cdot N_2Ph$, is prepared from β-naphthyltolylamine and diazobenzene chloride, and also forms deep-red needles with a metallic lustre; it is readily soluble in benzene and acetic acid, less so in alcohol and ether, and melts at 152°. On oxidation, it yields an ammonium base isomeric with the one obtained from the foregoing azo-compound, which is also best isolated as the *nitrate*. The latter forms short, slender, slightly-yellow needles which do not melt at 320°. The *picrate*,

$$C_{23}H_{17}N_3,C_6H_2(NO_2)_3 \cdot OH,$$

has a slightly darker colour than the isomeric salt, and melts at 206—207°. The *platinochloride*, $(C_{23}H_{17}N_3)_2.H_2PtCl_6$, also melts at a very high temperature, and forms a yellowish precipitate; and the *stannochloride*, $C_{23}H_{17}N_3,HSnCl_3$, crystallises in yellowish needles melting at 205—206.

Benzeneazo-αβ-dinaphthylamine, $C_{10}H_7{}^{\alpha}\cdot NH\cdot C_{10}H_6\cdot N_2Ph$, formed by acting on αβ-dinaphthylamine with diazobenzene chloride, always contains a violet-coloured impurity which is the hydrochloride of the isomeric diazo-compound. The latter may be decomposed by ammonia, and the product recrystallised from benzene, when the pure β-compound is obtained in woolly aggregates of deep-red needles melting at 167°. The oxidation requires great care, and then yields an ammonium base, whose *nitrate*, $C_{26}H_{17}N_3,HNO_3$, melts at 245—250° with decomposition. The *platinochloride*, $(C_{26}H_{17}N_3)_2,H_2PtCl_6$, forms a greyish-yellow precipitate, which is more soluble than the isomeric compound.

α-Naphthaleneazo-β-naphthylphenylamine, $NHPh\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_7{}^{\alpha}$, is formed from β-naphthylphenylamine and α-diazonaphthalene chloride without warming, and forms dark-red needles with metallic lustre which melt at 140°, and crystallise best from acetic acid. The ammonium base, obtained on oxidation, forms a *nitrate*, $C_{26}H_{17}N_3,HNO_3$, which crystallises in slightly-yellow needles, the melting point of which is above 320°. The *picrate*, $C_{26}H_{17}N_3,C_6H_2(NO_2)_3\cdot OH$, crystallises from acetic acid in short, hair-like needles melting at 270—271°, whilst the *platinochloride*, $(C_{26}H_{17}N_3)_2,H_2PtCl_6$, separates from acetic acid as a granular, crystalline precipitate.

β-Naphthaleneazo-β-naphthylphenylamine, $NHPh\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_7{}^{\beta}$, obtained from β-diazonaphthalene chloride, forms brick-red needles melting at 154—155°. The ammonium base formed by its oxidation is separated as the *nitrate*, $C_{26}H_{17}N,HNO_3$, which crystallises from alcohol in slender, yellowish needles melting above 320°. The *picrate*, $C_{26}H_{17}N_3,C_6H_2(NO_2)_3\cdot OH$, also forms slender, yellow needles which melt at 214°.

Benzeneazo-ββ-dinaphthylamine, $C_{10}H_7{}^{\beta}\cdot NH\cdot C_{10}H_6\cdot N_2Ph$, can only be prepared in the cold and in absence of an excess of acid, as otherwise the azine described below is obtained. It forms red needles or plates, soluble in alcohol and benzene, and melts at 139°. On oxidation, it does not yield an ammonium base, but forms the azine.

Symmetrical-ββ-naphthazine, $C_{10}H_6<\overset{N}{\underset{N}{|}}>C_{10}H_6$, is formed most readily by adding a strongly acid solution of diazobenzene chloride to a warm solution of ββ-dinaphthylamine, the azo-compound first formed decomposing in presence of acids into the azine and an aniline salt. It crystallises from hot alcohol or acetic acid in long, woolly, aggregates of slender, yellow needles which melt at 242—243°. Its solution in alcohol and acetic acid shows a strong blue, and in acetic acid a green fluorescence. H. G. C.

β-Dinaphthylcarbamide Chloride and β-Tetranaphthylcarbamide. By O. Kym (*Ber.*, 23, 1540—1543).—Kühn and Landau (this vol., p. 634) contradicted the author's statement (*ibid.*, p. 653) that β-dinaphthylcarbamide chloride cannot be conveniently prepared by the action of carbonyl chloride on β-dinaphthylamine at the ordinary temperature; but there is some mistake in their work, for they used a solution of 1 part of β dinaphthylamine in 30 parts of cold benzene, whilst the author finds that, at 14·5°, 92·3 parts of

benzene are required to dissolve 1 part of pure β-dinaphthylamine, and 70·6 for 1 part of the crude substance. However, he finds that when a solution of carbonyl chloride in toluene is allowed to remain in a closed vessel with a nearly saturated benzene solution of β-dinaphthylamine, crystals of the hydrochloride of the latter substance are slowly deposited, but the method is not an advantageous one for the preparation of β-dinaphthylcarbamide chloride.

β-Tetranaphthylcarbamide, $CO[N(C_{10}H_7)_2]_2$, was prepared by heating 2 grams of pure β-dinaphthylamine with 2·5 grams of β-dinaphthylcarbamide chloride in a test-tube, the final temperature being 260°. The resulting crystalline mass was crystallised from toluene, and then recrystallised from benzene. Small, sandy, ill-defined crystals were thus obtained, yellowish-white in colour, melting at 294—295°, and dissolving readily in benzene and toluene, but little in alcohol and acetic acid.

The substance obtained by Kühn and Landau by heating β-dinaphthylamine and β-dinaphthylcarbamide chloride with zinc-dust could not have been β-tetranaphthylcarbamide, for it melted at 167—169°, that is below β-dinaphthylamine and β-dinaphthylcarbamide chloride, whereas all tetralkyl carbamides melt at much higher temperatures than the corresponding dialkyl-amines and carbamide chlorides. C. F. B.

Action of Hydriodic Acid on 1 : 4′-Nitronaphthalenesulphonamide. By A. Eckbom (*Ber.*, **23**, 1118—1124).—Two products are obtained in this reaction, 1 : 4′-amidonaphthalenesulphonamide and 1 : 4′-diamidodinaphthyl bisulphide, according to the strength of the hydriodic acid; when the acid is very strong, the latter substance only is formed.

Amidonaphthalenesulphonamide, $[NH_2 \cdot C_{10}H_6 \cdot SO_2NH_2 = 1 : 4']$, is obtained by gently boiling nitronaphthalenesulphonamide with red phosphorus and excess of hydriodic acid (sp. gr. = 1·5) for six hours. The hydriodide crystallises out when the mixture is cooled; it is dissolved in alcohol, treated with sulphurous anhydride and then with ammonia, and the precipitated amide recrystallised from alcohol. It forms small, glittering, colourless tables melting at 259—260° to a brown oil, insoluble in water and cold alcohol, dissolving with difficulty in benzene, but more readily in acetic acid or hot alcohol. The *hydrochloride* crystallises partly in colourless, glittering scales, partly in star-like groups of needles; it is anhydrous. The *hydriodide* forms needles which are soluble in alcohol. The *acetonaphthalide*, obtained by treating the amide with the theoretical quantity of acetic anhydride, melts at 231—232°, and dissolves with difficulty in alcohol and water. The *diacetonaphthalide*, obtained by treating the amide with excess of acetic anhydride, forms thin scales melting at 200°. Both these compounds are anhydrous.

Diamidodinaphthyl bisulphide, $NH_2 \cdot C_{10}H_6 \cdot S \cdot S \cdot C_{10}H_6 \cdot NH_2$ $[NH_2 : S = 1 : 4']$, is found in the mother liquor after the amidonaphthalenesulphonamide has crystallised out. If nitronaphthalenesulphonamide is reduced with hydriodic acid of sp. gr. 1·96, diamidodinaphthyl bisulphide only is formed. It crystallises from alcohol in thin, lustrous,

colourless scales melting at 193° to a brown oil. It is found to be identical with the substance obtained by reducing dinitrodinaphthyl bisulphide, and must, therefore, have the constitution given above. The *hydrochloride* (with 2HCl) forms minute, colourless needles decomposed by water and alcohol. The *hydriodide* and the *sulphate* crystallise in needles. The *diacetonaphthalide* compound forms anhydrous, colourless scales melting at 274°, sparingly soluble in alcohol and water, more readily in acetic acid. The *dipropionaphthalide* compound, obtained by treating the amido-compound with propionic anhydride, forms anhydrous, colourless scales melting at 242°, insoluble in water, but soluble in acetic acid.

Amidonaphthalenesulphonamide, when heated at 140° for 2—3 hours in sealed tubes with red phosphorus and hydriodic acid (sp. gr. = 1·5), yields a substance crystallising in tables, which seems to be the hydriodide of *amidothionaphthol*. C. F. B.

Camphoric Acids. By J. E. Marsh (*Proc. Roy. Soc.*, **47**, 6—12). —When excess of phosphorus pentachloride is heated with camphoric acid on the sand-bath, *chlorocamphoryl chloride*, $C_{10}H_{13}Cl_3O_3$, is obtained. If, however, the temperature is not allowed to rise above that of boiling water, camphoryl chloride is the chief product of the reaction. This substance boils at 140° under 15 mm. pressure. When it is added gradually to 10 times its weight of hot water, about equal quantities of ordinary camphoric anhydride and a lævo-rotatory camphoric acid are formed, together with a small proportion of a more soluble substance, which appears to be a mixture of dextrogyrate camphoric acid and the new lævo-acid. The acid may be separated from the anhydride by treatment with sodium carbonate, in which the latter is insoluble. It dissolves, however, in hot caustic soda, and from the solution thus obtained the ordinary dextrorotatory acid is precipitated. On distillation, the lævo-acid gives the anhydride of the dextro-acid. Although the two acids have specific rotatory powers of $+48·25°$ and $-48·09°$ for the D-line, they are not merely optical isomerides; for the lævo-acid differs markedly in its ordinary properties from the dextro-acid, the melting points, for example, being 170° and 185° respectively. The mixture of the two isomerides, also, does not yield any definitely characterised compound. The camphoryl chloride from which both the acids are prepared is lævo-gyrate. To interpret his results, the author proposes the following geometrical formulæ for the two acids:—

$$C_5H_{10}\begin{array}{l}{}^{H}\!\!>C\cdot COOH \\ \quad\;\; | \\ {}_{H}\!\!>C\cdot CH_2\cdot COOH\end{array} \qquad \text{and} \qquad C_5H_{10}\begin{array}{l}{}^{COOH}\!\!>C\cdot H \\ \qquad\quad | \\ \quad\;\, {}_{H}\!\!>C\cdot CH_2\cdot COOH\end{array}.$$

The first formula appertains to the dextro-acid and its optically opposite isomeride—dextro- and lævo-ciscamphoric acids; the second formula represents the new lævo-acid and the corresponding dextro-isomeride—dextro- and lævo-transcamphoric acids. The two pairs are thus related to each other as maleïc acid is to fumaric acid. Lævo-transcamphoric acid would appear to be identical with the

lævo-acid obtained by Friedel from the so-called mesocamphoric acid. J. W.

Composition of Digitonin. By H. KILIANI (*Ber.*, **23**, 1555—1560).—According to Schmiedeberg, commercial digitalin contains, in addition to digitoxin, its most important pharmacological constituent, three glucosides, namely, digitonin, digitalin, and digitaleïn, the first in greater amount, and when heated with dilute acid, it yields a substance which reduces Fehling's solution, and also a crystalline compound insoluble in water, which he named digitogenin. The author dissolved 1 part of commercial digitalin in 10 parts of water, added 1 part of concentrated hydrochloric acid (sp. gr. 1·19), and heated the mixture for six hours on the water-bath. By this means, a solution and a light-grey precipitate were obtained. The solution contained about equal quantities of two glucoses, which were identified by means of the melting points of their osazones, and their behaviour when oxidised, as galactose and dextrose respectively. The precipitate of digitogenin was crystallised from alcohol, and found to be rather more than equal in amount to either of the two glucoses. It has the constitution $(C_5H_8O)_x$, probably $C_{15}H_{24}O_3$. Digitonin has, therefore, very probably the composition $C_{27}H_{44}O_{13}$, and its hydrolysis is expressed by the equation—

$$\underset{\text{Digitonin.}}{C_{27}H_{44}O_{13}} + 2H_2O = \underset{\text{Digitogenin.}}{C_{15}H_{24}O_3} + \underset{\text{Galactose.}}{C_6H_{12}O_6} + \underset{\text{Dextrose.}}{C_6H_{12}O_6}.$$

This would require a ratio of 1·4 : 1 : 1 between the weights of digitogenin, galactose, and dextrose formed; that actually found is more nearly 1 : 1 : 1. but it must be remembered that at the moment of hydrolysis digitogenin is much more easily attacked than galactose and dextrose, and very readily yields resinous products. An analysis of the raw material agreed well with the formula $C_{27}H_{44}O_{13}$; not so, however, did Schmiedeberg's analysis.

Digitogenin.—The following details may be added to Schmiedeberg's data regarding this substance. One part requires for solution 35 parts of boiling or 100 parts of cold 93 per cent. alcohol, and 20 parts of boiling or 30 parts of cold chloroform, and 30 parts of cold glacial acetic acid; it is insoluble in water and aqueous alkalis. It seems to form a compound containing chloroform of crystallisation, which loses its chloroform only very slowly at 110°. With alcoholic potash, it forms a crystalline potassium compound, strongly alkaline, and little soluble in alcohol. It forms no stable compounds with barium hydroxide or phenylhydrazine, but is attacked by mineral acids and oxidising agents. C. F. B.

Brazilin. By C. SCHALL and C. DRALLE (*Ber.*, **23**, 1428—1437; compare Abstr., 1889, 55, 1004).—On treating the dibromobrazileïn bromides with zinc-dust and acetic acid, part of the halogen is eliminated; with acetic anhydride, instead of acetic acid, acetyl-derivatives are obtained. The following compounds have been prepared in this manner; they are amorphous or slightly crystalline powders, ranging in colour from dark brown to yellowish-brown;

they contain about 1 mol. H_2O, which is driven off by heating at 140°. *Dibromoacetylbrazileïn*, $C_{16}H_9Br_2O_5Ac$, from octobromobrazileïn; *dibromodiacetylbrazileïn*, $C_{16}H_8Br_2O_5Ac_2$, from hexabromobrazileïn; *dibromotriacetylbrazileïn*, $C_{16}H_7Br_2O_5Ac_3$, from monobromobrazileïn; *dibromotetracetylbrazileïn*, $C_{16}H_6Br_2O_5Ac_4$, from tetrabromobrazileïn; *tribromobrazileïn*, $C_{16}H_9Br_3O_5$, from octobromobrazileïn; *tribromotetracetylbrazileïn*, $C_{16}H_5Br_3O_5Ac_4$, from hexa- and octobromobrazileïn.

An amorphous modification of brazilin tetramethyl ether is obtained by cooling the molten crystalline modification, or by precipitating from acetic acid solution with water; it melts at 82—86°, and is at once converted into the crystalline modification by heating at 89°, or more slowly at ordinary temperatures. The refraction equivalent of this compound indicates the existence of six double bonds. *Dibromobrazilin tetramethyl ether*, $C_{16}H_8Br_2(OMe)_4$, is obtained by treating an alcoholic solution of the ether with a glacial acetic acid solution of bromine at ordinary temperatures; it melts at 215°, and is insoluble in alkalis. A 20 per cent. solution of brazilin tetramethyl ether in glacial acetic acid is mixed with a 10 per cent. solution of bromine in the same menstruum, the mixture is first cooled, then heated nearly to boiling; in this way two compounds are formed, the one speedily separates in brilliant, red crystals, the other is deposited more slowly. The red substance appears to be a *dibromobrazilin tetramethyl ether dibromide*, $C_{16}H_8Br_2O(OMe)_4Br_2$, isomeric with the reddish-brown compound described in a previous paper. The second compound formed in the above experiment is *bromobrazilin tetramethyl dibromide*, $C_{16}H_7BrO(OMe)_4Br_2$.

It has been found that brazileïn may easily be prepared by treating a 30 per cent. solution of brazilin in glacial acetic acid, with an equal molecular proportion of potassium nitrite; after remaining for several hours, crystals of pure brazileïn are deposited; the yield is 70 per cent. of the brazilin employed. Hæmateïn is obtained in a similar manner from hæmatoxylin.

Brazileïndihydroxime, $C_{16}H_{10}O(OH)_2(NOH)_2$, is obtained by heating an alcoholic solution of brazileïn with excess of hydroxylamine in a sealed tube. The substance is very insoluble, and could not be recrystallised. *Brazileïnphenylhydrazone*, $C_{16}H_{12}O_4{:}N_2HPh$, is obtained by boiling brazileïn with phenylhydrazine; after purification, the compound is obtained as a dark brown powder which does not melt; it is soluble in alkalis. During the preparation of this compound, a considerable evolution of ammonia occurs, which probably indicates the presence of an alcoholic group in brazileïn.

A comparison of specimens of brazileïn, prepared by each of the four known methods, shows that the compounds are identical: (*a*) in the silvery lustre and form of the crystals; (*b*) in the melting point and crystalline form of the acetyl compound, $C_{16}H_9O_5Ac_3 + 2C_2H_4O_2$; (*c*) in the identity of the substances obtained by three different methylation processes; these facts prove, therefore, that there is only one brazileïn.

J. B. T.

Diastase considered as a Mixture of Maltase and Dextrinase. By H. P. Wijsman, Jun (*Rec. Trav. Chim.*, **9**, 1—13; compare also Lintner and Eckhardt, this vol., 519, and Brown and Morris, Trans., 1890, 507).—The author starts with the assumption that the diastase of malt is composed of a mixture of two enzymes—*maltase* and *dextrinase*. The former converts starch into a mixture of maltose and a dextrin coloured violet by iodine, and corresponding with the erythro-granulose of various workers; the latter enzyme converts starch into a dextrin which reduces Fehling's solution, is not coloured by iodine. and corresponds with the maltodextrin of Herzfeld and of Brown and Morris. Maltodextrin is converted into maltose by maltase, and when dextrinase acts on erythro-granulose, a dextrin is formed which does not reduce Fehling's solution, and is not coloured by iodine—this dextrin the author terms *leucodextrin*.

The following experiments are quoted in proof of the above theory. A diastase was prepared by fractionally precipitating with alcohol of 97 per cent., a malt-extract, made with 20 per cent. alcohol, and purifying the precipitate by repeated solution and precipitation. The method employed to show the presence of two enzymes in this preparation consisted of partial separation by diffusion into a gelatinous mass, made by adding gelatin to a solution of Lintner's soluble-starch. When a small quantity of diastase solution was placed on a layer of the solidified starch solution, the progress of the hydrolysing action of the former could be traced by means of iodine solution, it being found that after 1—2 days' action the diffusion-field of the diastase formed a colourless zone bordered by a violet ring, whilst the gelatin with unaltered starch was coloured deep blue. From this the author assumes that the two enzymes diffuse into the gelatin mixture at different rates depending on their relative concentrations, and the violet-coloured ring denotes the space in which the maltase has penetrated beyond the dextrinase, whilst in the non-coloured inner zone both enzymes are present. When a portion of the violet-coloured ring was removed, and placed on a fresh portion of starch-gelatin, and the enzyme allowed to diffuse, no non-coloured zone was observed. the whole of the product of the action being coloured violet by iodine. The author also mentions, as a proof of his theory, the known fact that alcohol, heat, acids, &c., have a differential action on diastase: maltase and dextrinase being influenced to a greater or lesser extent by these reagents.

The formation of maltose was proved by means of *Photobacterium phosphorescens*, Beijerinck, which develops phosphorescence by the oxidation and assimilation of certain foods, of which maltose is one. Starch and the dextrins are not able to bring about the phosphorescence. By means of the starch-gelatin method, used in conjunction with this bacterium, the author considers that he proves the formation of maltodextrin by the action of dextrinase, and the subsequent conversion of this into maltose by the action of maltase. G. H. M.

Nature of Gum-ferments. By F. Reinitzer (*Zeit. physiol. Chem.*, **14**, 453—470).—The gum-ferment described by Wiesner (*Sitz. Wiener Akad.*, **92** (1885), 40) in various species of gum is not

the cause of the formation either of gum or plant mucilage. It cannot change cellulose into gum or mucilage, but it converts starch paste to a considerable extent (40 per cent. of the dried starch) into a reducing sugar, with the probable simultaneous formation of a dextrin. The small quantity of sugar almost always found in gum-arabic is probably the result of this action. Wiesner further considers that Reischl's gum test (*Ber. österr. Ges. Ford. Chem. Ind.*, **1** (1879), 74), which consists in boiling with orcinol and hydrochloric acid, depends for its occurrence on the presence of gum-ferment. This is also erroneous. Its occurrence is really due to the carbohydrate itself, and is probably explained by the fact that boiling it with the acid gives rise to furfuraldehyde, which yields the blue colour with orcinol.

Pepsin which is completely free from carbohydrate material does not give a coloured precipitate with these reagents. Diastase purified by precipitation with alcohol gives only a small quantity of the precipitate, and this is probably due to adherent traces of dextrin.

The ferment itself has hitherto only been obtained with certainty from gum-acacia, cherry gum, from a few rarer gums, and from certain tissues of various kinds of stone-fruit, being absent in all the other tissues. Its occurrence in mucilage-yielding tissues, and in wood is very doubtful; tragacanth, however, appears often to contain it; but it is absent in plant mucilage. The darker kinds of gum-acacia appear to contain it more abundantly than the lighter varieties.

W. D. H.

Action of Acetone on Pyrroline. By M. DENNSTEDT (*Ber.*, **23**, 1370—1374).—The condensation-product of acetone and pyrroline first observed by Baeyer, and further examined by the author and Zimmerman (Abstr., 1887, 598, 1052), has a molecular weight, as determined by Raoult's method, twice as great as has been hitherto supposed. Its formula is therefore $C_{28}H_{36}N_4$, instead of $C_{14}H_{18}N_2$ It has previously been shown that the compound splits up on dry distillation into pyrroline, isopropylpyrroline, and a pyrroline of the composition $C_{10}H_{13}N$, boiling at about 275°. The constitutional formula previously assigned to this compound is not in agreement with the results described in this paper, and the author now regards it as a condensation-product of 2 mols. acetone and 1 mol. pyrroline, that is, as a mesitylpyrroline, which has possibly the following constitution, $HC{<}{\begin{matrix}CH\cdot C\\ \quad\ \| \\ NH\cdot C\end{matrix}}{>}CMe\cdot CH{:}CMe_2$.

Besides these products, a quantity of higher boiling oil has been obtained from the decomposition-products. It readily becomes brown in the air, is not readily volatile with steam, but otherwise shows all the characteristic properties of the pyrroline-derivatives. On account of its high boiling point it could not be purified, but the analysis showed it to be very rich in carbon, and it was also found to yield a 1′-acetyl compound boiling above 360°. On reduction with tin and hydrochloric acid, it yields a *stannochloride* of the composition $C_{13}H_{19}N,HSnCl_3$, which forms well-developed, slightly-yellow crystals, becomes dark at 150°, and melts to a brown liquid at 170°. The base is set free by alkali, and may be distilled off in a current of steam. It

is a yellowish liquid, lighter than water, which has a characteristic odour and boils at 274°. Its *hydrochloride*, $C_{13}H_{19}N,HCl$, forms compact crystals or thick needles melting at 227—228°. The *platinochloride* and *aurochloride* are precipitated by adding platinic or gold chloride to the solution of the hydrochloride, but the first named decomposes in a short time and the latter immediately with deposition of platinum and gold respectively.

The composition of this reduction-product renders it probable that the formula of the original substance is $C_{13}H_{17}N$, which is probably a *phoronpyrroline*, and may have the constitution

$$HC{<}{\begin{matrix}CH\cdot C\\ NH\cdot C\end{matrix}}{>}CMe\cdot CH{:}CMe\cdot CH{:}CMe_2.$$

Mesitylpyrroline, $C_{10}H_{13}N$, may also be reduced in a similar manner, but the hydrochloride is hygroscopic, and the stannochloride does not crystallise, so that the compounds have not yet been obtained in a pure condition.

H. G. C.

Condensation-products of α-Acetylpyrroline with Benzile. By A. Angeli (*Ber.*, **23**, 1355—1357).—Like the fatty and aromatic ketones, α-acetylpyrroline readily forms condensation-products with benzile. When the two substances mixed in equal molecular proportions are heated with concentrated aqueous potash on the water-bath, two products are obtained, one of which may be collected on cooling, and recrystallised from benzene, the solution being previously heated with animal charcoal. It forms small, yellow, lustrous plates which melt at 184°, and have the formula $C_{20}H_{15}NO_2$. The second compound is obtained by acidifying the alkaline solution, and recrystallising the precipitate first from alcohol, then from benzene, and finally from alcohol again. It then forms hard, colourless crystals which have the composition $C_{20}H_{17}NO_3$, and melt at 216°.

The constitution of these compounds is readily explained by analogy with the compounds obtained by Japp and Miller (Trans., 1885, 11) from benzile and acetophenone. The first compound corresponds with triphenylcrotolactone, and may be termed *diphenylpyrroylcrotolactone*, ${\begin{matrix}CPh\cdot CH\\ CO — O\end{matrix}}{>}C\cdot C_4NH_4$. By the action of alkalis this then takes up water and passes into the second compound, which is *α-diphenyl-β-pyrroylpropionic acid*, $C_4NH_4\cdot CO\cdot CH_2\cdot CPh_2\cdot COOH$.

Pyrryl methyl ketone also combines with ethyl salts. Ethyl oxalate in this manner yields *ethyl pyrroylpyruvate*,

$$C_4NH_4\cdot CO\cdot CH_2\cdot CO\cdot COOEt.$$

H. G. C.

Dimethylpyrrolidine and Diamidohexane. By J. Tafel and A. Neugebauer (*Ber.*, **23**, 1544—1550).—A further examination of these compounds, which were obtained by the reduction of the diphenylhydrazone of acetonylacetone (Abstr., 1888, 1015), has shown that the formulæ assumed for them, ${\begin{matrix}CH_2\cdot CHMe\\ CH_2\cdot CHMe\end{matrix}}{>}NH$ and $NH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHMe\cdot NH_2$ respectively, are correct.

Diamidohexane, $NH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CHMe\cdot NH_2$, may be prepared by warming an alcoholic solution of acetonylacetone, reducing it directly with sodium amalgam and acetic acid, and separating the two basic products as before described. The following salts were prepared:—*Hydrochloride*, $C_6H_{16}N_2,2HCl$, colourless needles, sparingly soluble in alcohol. *Platinochloride*, $C_6H_{16}N_2,H_2PtCl_6$, aggregates of small plates, sparingly soluble in alcohol, and decomposing at 238° without melting. *Aurochloride*, $C_6H_{16}N_2,2HAuCl_4$, golden prisms easily soluble in alcohol. *Carbonate*, $\begin{array}{l} CH_2\cdot CHMe\cdot NH\cdot CO \\ | \qquad\qquad\qquad\quad | \\ CH_2\cdot CHMe\cdot NH_3\cdot O \end{array}$, a white, crystalline substance soluble in water and alcohol, but not in ether, and decomposing at about 100°; prepared by passing carbonic anhydride into an ethereal solution of diamidohexane.

When diamidohexane hydrochloride is rapidly distilled, ammonium chloride, dimethylpyrrolidine hydrochloride, and unchanged diamidohexane hydrochloride distil over. The mixture is distilled with potash, when ammonia is first evolved; the bases then distil over, and are dried over baryta and separated by fractionation.

2 : 5-*Dimethylpyrrolidine*, $\begin{array}{l} CH_2\cdot CHMe \\ | \\ CH_2\cdot CHMe \end{array}\!\!>NH$. The oxalate and platinochloride have already been described. The *hydrochloride* forms colourless needles melting at 188—190°. *Nitrosodimethylpyrrolidine* was obtained by the action of sodium nitrite on a solution of dimethyl pyrrolidine in excess of sulphuric acid. It is a yellow oil boiling at 135° at 60 mm. pressure, slightly soluble in water, and separated from the solution by alkalis, alkaline carbonates, and sodium chloride. Easily soluble in ether, alcohol, chloroform, benzene, and 50 per cent. acetic acid; also in light petroleum and cold sulphuric acid, but decomposing when this last solution is warmed. When reduced with zinc-dust and dilute acetic acid, it yields dimethylpyrrolidine, and also the *hydrazine compound* of this substance. This was oxidised by means of mercuric oxide to the *tetrazone*, $(C_6H_{12})_2N_4$, which melts at 43°, and distils without decomposing. It dissolves easily in alcohol, ether, benzene, light petroleum, and chloroform, also in dilute acids; but these solutions decompose it when warmed.

1 : 2 : 5-*Trimethylpyrrolidine*, $\begin{array}{l} CH_2\cdot CHMe \\ | \\ CH_2\cdot CHMe \end{array}\!\!>NMe$, is formed, together with its methyl iodide additive compound, when dimethylpyrrolidine in cooled ethereal solution is treated with methyl iodide and allowed to remain for several hours, the product being finally treated with potash. It is separated from unchanged dimethylpyrrolidine, and purified; it then boils at 115—116° under 750 mm. pressure. Its *hydrochloride*, $C_7H_{16}NCl$, forms brilliant, white prisms; the *platinochloride* a yellow, uncrystallisable oil, little soluble in alcohol. The *methiodide*, $C_8H_{18}NI$, is formed with much evolution of heat by adding methyl iodide to the base. It dissolves in water, and less easily in alcohol, from which it crystallises out in well-formed, colourless prisms melting at 255—256°. When heated with solid potash, it yields dimethylamidohexylene.

Dimethylamidohexylene, $CHMe{:}CH\cdot CH_2\cdot CHMe\cdot NMe_2$, is a strongly

alkaline liquid, boiling at about 130°, smelling like the pyrrolidine-derivatives, and little soluble in water. It yields by direct addition a *methiodide*, $C_9H_{20}NI$, melting at 187°. C. F. B.

Pyridine-derivatives from Propaldehyde and Propaldehyde-ammonia. By E. DÜRKOPF and H. GÖTTSCH (*Ber.*, **23**, 1110—1112).—An addition to a previous paper (this vol., p. 794). Waage's parvoline is shown to have the formula [Et : Me_2 = 2 : 3 : 5] in the following manner :—(1) when oxidised, it yields carboxydinicotinic acid, and must therefore have its alkyl-groups in the positions 2 : 3 : 5; (2) the dimethylpyridinecarboxylic acid obtained by oxidation of Waage's parvoline yields, when distilled with lime, a lutidine which has been shown (see next abstract) to have the methyl-groups in the positions 3 : 5.

The methylpyridinedicarboxylic acid, [$(COOH)_2$: Me = 2 : 3 : 5 or 2 : 5 : 3], obtained by further oxidation of Waage's parvoline, gives off carbonic anhydride at 225° when heated with acetic acid and anhydride, and forms a white mass of β-methylnicotinic acid, [COOH : Me = 3 : 5], melting at 214—216°, and soluble in water.

The parvoline boiling at 216—217°, when oxidised, yields a dimethylpyridinedicarboxylic acid, which, when carefully purified, formed yellowish, sparingly soluble needles melting at 258°, giving no coloration with ferrous sulphate, but forming a precipitate with mercurous nitrate, and with concentrated solutions of copper salts. In these properties it agrees with the $\alpha\gamma$-dimethyldinicotinic acid described by Weber (Abstr., 1887, 1117), but it is anhydrous, whereas Weber's acid crystallised with 2 mols. H_2O. If, however, these two compounds are identical, then the parvoline boiling at 216—217° is a tetramethylpyridine of the constitution [Me_4 = 1 : 2 : 3 : 4]. C. F. B.

A New Lutidine. By E. DÜRKOPF and H. GÖTTSCH (*Ber.*, **23**, 1113—1114).—The base obtained from dimethylpyridinecarboxylic acid (preceding abstract) boils at 169—170°, and is shown to be a *lutidine* of the constitution $C_5NH_3Me_2$ [Me_2 = 3 : 5], for when oxidised with a cold dilute solution of permanganate, it yields dinicotinic acid, $C_5NH_3(COOH)_2$ [$(COOH)_2$ = 3 : 5], crystallising in small, anhydrous needles, soluble in water, and melting at 314—315° (uncorr.). This lutidine is a clear, strongly refracting liquid, moderately soluble in cold water, less so in warm; its sp. gr. at 0° is 0·9614, water at 4° being 1. The *platinochloride*, $(C_5NH_3Me)_2,H_2PtCl_6$, forms dark-red needles and plates melting with decomposition at 255—256°. The *aurochloride*, $C_5NH_3Me_2,HAuCl_4$, forms yellow needles melting at 149°, and little soluble in water. The *mercurochloride* forms long needles melting at 170°, and sparingly soluble in water. A small quantity of this lutidine is also formed by the action of propaldehyde-ammonia on propaldehyde. C. F. B.

Piperidine Bases. By E. LELLMANN and M. BÜTTNER (*Ber.*, **23**, 1383—1388).—It has been shown by Lellmann (Abstr., 1887, 604) that bromobenzene readily acts on piperidine at 250°, with elimination of hydrogen bromide and formation of tertiary phenylpiperidine.

The authors have extended the investigation to the action of piperidine on other halogen-derivatives of aromatic hydrocarbons, and find that a similar action takes place in all cases. The reaction was carried out in a sealed tube, heated in most cases to 250—260°.

Tertiary-α-naphthylpiperidine, $C_{10}H_7 \cdot C_5NH_{10}$, is obtained as a thick, yellow oil boiling at 185—190° under 5—10 mm. pressure, and having a slightly fæcal odour. It dissolves readily in alcohol, ether, and benzene, and yields a *hydrochloride* which is readily soluble in water, and crystallises in fascicular aggregates of needles. Its *platinochloride*, $C_{15}H_{17}N,H_2PtCl_6 + 2H_2O$, is a sparingly soluble precipitate.

Tertiary β-naphthylpiperidine, $C_{10}H_7 \cdot C_5NH_{10}$, crystallises from light petroleum in nodular aggregates of small prisms melting at 57—58°, which become grey on standing. The *platinochloride* is a pale-yellow precipitate which has the composition $C_{15}H_{17}N,H_2PtCl_6 + 6H_2O$.

Tertiary anthracylpiperidine, $C_{14}H_9 \cdot C_5NH_{10}$, is obtained as a yellow precipitate which is very quickly oxidised in the air. Its *platinochloride*, $C_{19}H_{19}N,H_2PtCl_6 + 2H_2O$, is a yellow precipitate which also becomes red in the air.

Tertiary phenanthrylpiperidine, $C_{14}H_9 \cdot C_5NH_{10}$, crystallises from ether in nodular aggregates melting at 113°. Its *platinochloride*, $C_{19}H_{19}N,H_2PtCl_6 + 6H_2O$, is soluble with difficulty in water.

Paranitro-α-naphthylpiperidine, $NO_2 \cdot C_{10}N_6 \cdot C_5NH_{10}$, obtained by the action of 1 : 4-bromonitronaphthalene on piperidine, crystallises from alcohol in long, yellow needles melting at 77°. It is a very feeble base, the salts of which are at once decomposed by water.

Piperydylrhodamine, $CO{<}{\substack{C_6H_4\\O—}}{>}C{<}{\substack{C_6H_3(C_5NH_{10})\\C_6H_3(C_5NH_{10})}}{>}O$, is obtained in almost the theoretical quantity, by heating fluoresceïn chloride with piperidine at 220°. If forms a violet, flocculent precipitate which is soluble in alcohol, and very stable towards alkalis. The *hydrochloride*, $C_{30}H_{30}O_3N_2,2HCl$, is very readily soluble in water, the dilute solution having a bluish-red tinge, whilst concentrated hydrochloric acid colours it yellow. The *platinochloride* and *aurochloride* are amorphous, violet precipitates. H. G. C.

β-Methylpiperidine Bases. By E. Lellmann and M. Büttner (*Ber.*, **23**, 1388—1390).—Whereas piperidine acts very readily with halogen-derivatives of hydrocarbons (compare preceding abstract), it has been found in the course of an investigation which will shortly be published, that α-methylpiperidine and coniïne have very little tendency to undergo this reaction, owing seemingly to the proximity of the alkyl-group to the nitrogen-atom. The authors find that β-methylpiperidine undergoes this reaction much more readily than the α-compound, but, as might be expected, less readily than piperidine.

Paranitrophenyl-β-methylpiperidine,

$$NO_2 \cdot C_6H_4 \cdot C_5NH_9Me\ [NO_2 \cdot C_6H_4 : Me = 1 : 3],$$

is prepared by heating parachloronitrobenzene with β-methylpiperidine for five hours. It crystallises from alcohol in small, golden

plates, and from light petroleum in yellow prisms which have a pale-blue surface colour, and melt at 61°. The *hydrochloride* forms colourless needles which are partially decomposed by water; the *platinochloride* forms lustrous, brownish-red crystals, fairly soluble in water; and the *aurochloride*, $C_{12}H_{16}N_2O_2,HAuCl_4 + 2H_2O$, small, pale-yellow needles which melt with decomposition above 55°.

Orthoparadinitrophenyl-β-methylpiperidine, $C_6H_3(NO_2)_2 \cdot C_5NH_9Me$, is obtained in a similar manner from ordinary dichloronitrobenzene. It forms beautiful, yellow needles melting at 67°, and readily soluble in alcohol, ether, and benzene.

β-Methylpiperidine also acts on bromobenzene and α-bromonaphthalene, but less readily than piperidine. H. G. C.

Quinoline-ring Formation: Constitution of Benzene. By W. Marckwald (*Ber.*, **23**, 1015—1025).—The synthesis of quinoline-derivatives by Skraup's reaction affords a means of deciding between Dewar's, Kekulé's, and Baeyer's formulæ for benzene. If Dewar's formula expresses the constitution of benzene, meta- and para-phenylenediamine should yield quinoline-derivatives of a constitution analogous to that of anthracene-derivatives; if Kekulé's formula is the true one, the quinoline-derivatives obtained should have a phenanthrene-like structure; if Baeyer's centrical formula is the true one, two isomerides might be formed from each of the diamines.

As a matter of fact, they both yield quinoline-derivatives having the phenanthrene-like structure, and no isomerides are formed in the reaction, so that Dewar's benzene formula is inadmissible.

A quinoline-derivative having a phenanthrene-like structure is also obtained from β-naphthylamine, and all β-naphthaquinolines have an analogous constitution.

The formation of a quinoline-derivative from α-bromo-β-amidonaphthalene with elimination of hydrogen bromide, and from α-nitro-β-amidonaphthalene with elimination of nitrous acid, are reactions which tend to show the inadmissibility, not only of Dewar's, but also of Baeyer's benzene formula, whereas they are in complete accordance with that of Kekulé.

These considerations have led the author to investigate the behaviour of paraxylylenediamine with glycerol, nitrobenzene, and concentrated sulphuric acid; the constitution of this diamine is such that if Baeyer's or Dewar's benzene formula is correct, two quinoline-rings must be formed in the reaction, whereas if benzene has the constitution expressed by Kekulé's formula, the formation of two quinoline-rings would be impossible.

The experiments, which were carried out under varied conditions, have shown that amidodimethylquinoline is the only product of the reaction.

Amidodimethylquinoline, $[Me_2 : NH_2 = 1 : 4 : 3]$, crystallises from hot dilute alcohol in yellow needles, melts at 175°, with previous softening, and is almost insoluble in hot water and light petroleum, and only sparingly soluble in cold alcohol, but readily in ether, benzene, chloroform, acetone, and hot alcohol. It has a slight aromatic odour, and is only very slightly volatile with steam, but it sublimes in beauti-

ful, yellow crystals. The salts are yellow or red, crystalline compounds, generally readily soluble in water, but only sparingly soluble in alcohol; very dilute solutions of the salts impart to a pine-chip an intense, reddish-yellow coloration, and give a reddish-brown, semi-crystalline precipitate with mercuric salts. The *hydrochloride*, $C_{11}H_{12}N_2,2HCl$, decomposes at 100°; the *platinochloride*,

$$C_{11}H_{12}N_2,H_2PtCl_6,$$

crystallises in needles, and is partially decomposed by water. The *sulphate*, *nitrate*, and *dichromate* crystallise in needles; the *picrate*, $C_{11}H_{12}N_2,2C_6H_3N_3O_7$, decomposes slowly at 182°. The *acetyl*-derivative, $C_{11}H_{11}N_2Ac$, crystallises in microscopic needles, melts at 212°, and sublimes without decomposition; it is readily soluble in alcohol, but only sparingly in ether, light petroleum, and benzene, and insoluble in water; it yields a crystalline *platinochloride*, a crystalline *aurochloride*, and a crystalline *picrate*, $C_{11}H_{11}N_2Ac,C_6H_3N_3O_7$, which melts at 223—224°.

Phenyldimethylquinolylthiocarbamide, $NHPh·CS·NH·C_{11}NH_{10}$, prepared by treating amidodimethylquinoline with phenylthiocarbimide, separates from hot alcohol as a yellowish, crystalline powder, melts at 157—159° with previous softening, and is readily soluble in hot alcohol and benzene, but only moderately easily in ether, and insoluble in water and light petroleum. It dissolves freely in mineral acids, but is partially reprecipitated on the addition of water; the *platinochloride*, $(C_{18}H_7N_3S)_2,H_2PtCl_6$, and the *aurochloride* are crystalline. F. S. K.

Colouring Matters from Tetradihydroquinoline. By E. LELLMANN and H. BOYE (*Ber.*, **23**, 1374—1383).—It has previously been shown (Abstr., 1888, 1108) that paramidophenylpiperidine gives all the colour reactions of paramidodimethylaniline and its homologues. The former may be regarded as having been derived from amidoethylpropylaniline by the loss of two atoms of hydrogen with formation of a closed chain or ring.

Researches which will shortly be published have shown that paradiamidodiphenylpiperazine, which may be regarded as having been derived in a similar manner from two molecules of amidodimethylaniliue, also yields indamine colours when treated in the same manner.

Tetrahydroquinoline may also be regarded as derived from ethylorthotoluidine by elimination of two atoms of hydrogen and formation of a closed chain, and the authors have therefore examined the behaviour of this compound with regard to the formation of colouring matters, and have found that it can in fact be readily converted into indamine and azo-derivatives.

By the action of the theoretical quantity of potassium dichromate on a mixture of the hydrochlorides of amidodimethylaniline and tetrahydroquinoline in equal molecular proportions, or allowing the hydrochlorides of the latter compound and of paranitrosodimethylaniline to remain together in aqueous solution, an indamine is obtained which

has doubtless the constitution $NMe_2{\cdot}C_6H_4{\cdot}N{<}\begin{array}{l}C_6H_3{\cdot}CH_2\\ N{-}{-}CH_2\end{array}{>}CH_2$. This compound readily passes without change of composition into a leuco-base.

It is probable that this property is due to the fact that two atoms of hydrogen in the piperidine-ring are given off, and that they then act on the colouring matter forming the leuco-base, which would on this supposition have the constitution

$$NMe_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_3{<}\begin{array}{l}CH_2{\cdot}CH\\ NH\,{\cdot}CH\end{array}.$$

On oxidation, the leuco-base is converted into a new indamine containing two atoms of hydrogen less than the first compound, and this in the same manner passes after a time into an isomeric leuco-base, $NMe_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_3{<}\begin{array}{l}CH{\cdot}CH\\ N{-}CH\end{array}$, which must be a derivative of quinoline.

These reactions have been followed, not on the above compound, but on the corresponding *tetrahydroquinolinedimethylanilinethiosulphonic indamine*, obtained, according to Bernthsen's method (Abstr., 1889, 776), by the oxidation of tetrahydroquinoline and amidodimethylanilinethiosulphonic acid. It has the constitution

$$NMe_2{\cdot}C_6H_3(SSO_3H){\cdot}N{<}\begin{array}{l}C_6H_3{\cdot}CH_2\\ N{-}{-}CH_2\end{array}{>}CH_2.$$

The leuco-compound into which it passes on standing is not colourless, but has a brown colour.

The colouring matter, which may be shortly termed "tetrahydroindamine," is readily acted on by zinc-dust and hydrochloric acid, with evolution of hydrogen sulphide and formation of a leuco-base, which on oxidation with ferric chloride yields a colouring matter of the methylene-blue series; this has the constitution

$$\begin{array}{c}S{-}{-}C_6H_2{-}CH_2\\ NMe_2{\cdot}C_6H_3{\cdot}N_2{\cdot}CH_2{\cdot}CH_2\end{array}.$$

The tetrahydro-blue, which in its colour closely resembles methylene-blue, is faster than tetrahydro-indamine; thus, after several months, no external change was noticeable in the substance itself, although the fibres dyed with it gradually became paler.

The leuco-base of the dihydroindamine obtained from tetrahydroindamine is decomposed by continued boiling with water, with formation of a new leuco-base, which on oxidation yields a "dihydro-blue," probably having the constitution $\begin{array}{c}S{-}{-}C_6H_2{-}CH_2\\ NMe_2{\cdot}C_6H_3{\cdot}N_2{\cdot}CH{:}CH\end{array}$. Its leuco-base, unlike that of the tetrahydro-blue, is scarcely oxidised by the air, and on reduction with zinc-dust and hydrochloric acid, appears to be converted into the latter compound.

Methyltetrahydroquinoline (kairoline) is also oxidised in presence of amidodimethylanilinethiosulphonic acid to an indamine resembling

in most respects those already described, but which may be recrystallised from water without alteration. H. G. C.

Ethanediquinolyline. By A. M. Comey (*Ber.*, **23**, 1115—1117).—Dibenzyl was prepared by heating benzyl chloride with sodium for 3—4 hours in a reflux apparatus over the bare flame, and then distilling off the dibenzyl. It was then converted into paradinitrobenzyl, and this was reduced with tin and hydrochloric acid. The paradiamidodibenzyl obtained was cautiously heated with nitrophenol, sulphuric acid, and glycerol in a reflux apparatus; the mixture solidified on cooling, and was then treated with much hot water, deprived of excess of phenol by means of a current of steam, and treated with aqueous soda. A brown, tarry mass separated; it was boiled with toluene, and the toluene evaporated from the solution, the base being thus obtained as a brown, crystalline mass. This was dissolved in dilute sulphuric acid, and alcohol was added; ethanediquinolyline was thus precipitated as the normal sulphate, which was dissolved in very dilute sulphuric acid, boiled two or three times with animal charcoal, and then decomposed with aqueous soda. *Ethanediquinolyline*, $C_2H_4(C_9NH_6)_2$ [$C_2H_4 = 3$], thus obtained forms colourless, hexagonal plates melting at 124°, soluble in ether, alcohol, benzene, and toluene, but insoluble in water. The *dihydrochloride*, $C_{20}H_{16}N_2,2HCl + 4H_2O$, forms silky needles. very soluble in water, which readily lose their water of crystallisation, but not their hydrogen chloride, when dried over sulphuric acid. The *sulphate* forms stout prisms, dissolving easily in hot water, slightly in cold, and insoluble in alcohol. The *platinochloride*, $C_{20}H_{16}N_2,H_2PtCl_6$, forms a mass of minute crystals, insoluble in cold water. The *aurochloride*, $C_{20}H_{16}N_2,2HAuCl_4$, forms a yellow precipitate, also insoluble in cold water. C. F. B.

Formation of α- and β-Phenylenepyridineketonecarboxylic Acids by the Oxidation of Naphthaquinoline-derivatives. By O. Doebner and J. Peters (*Ber.*, **23**, 1228—1242).—α-Phenylenepyridineketone and some of its derivatives have already been obtained by Skraup and Cobenzl (Abstr., 1883, 1010) and by Doebner and Kuntze (Abstr., 1889, 411) by the oxidation of α-naphthaquinoline and of α-naphthacinchonic acids. The authors find that they may be very readily prepared by the oxidation of α-cinnamenylnaphthacinchonic acids, which may be obtained in a similar way to the α-cinnamenylcinchonic acids (Doebner and Peters, this vol., p. 176).

α-Cinnamenyl-α-naphthacinchonic acid, $CHPh{:}CH{\cdot}C{<}^{N—C_{10}H_6}_{CH{:}C{\cdot}COOH}$, may be prepared by dissolving cinnamaldehyde (1 mol.) and pyruvic acid (1 mol.) in ether, and adding an ethereal solution of α-naphthylamine (1 mol.), cooling well during the addition. The reaction may be also carried out in warm alcoholic solution. The acid separates in a few hours in slender, yellow crystals, which are collected, washed with ether, and recrystallised from acetic acid. It then forms slender, citron-yellow needles which melt with decomposition at 256°, are insoluble in water, sparingly soluble in ether, chloroform, and benzene, more readily in alcohol and acetic acid. The

alkaline salts form fascicular aggregates of silky needles, readily soluble in water, whilst the salts of the alkaline earths form flocculent precipitates, the *barium* salt, $(C_{22}H_{14}NO_2)_2Ba$, containing 2 mols. of water. The *copper* salt, $(C_{22}H_{14}NO_2)_2Cu + H_2O$, is a greenish-yellow, flocculent precipitate; and the *silver* salt, $C_{22}H_{14}NO_2Ag$, a voluminous, yellow powder.

α-Cinnamenyl-α-naphthaquinoline, $CHPh{:}CH{\cdot}C{\Large<}{\begin{matrix}N-C_{10}H_6\\ CH{:}CH\end{matrix}}$, is obtained from the foregoing compound by heating it alone or with soda-lime; a reddish oil distils over which solidifies on allowing its ethereal solution to evaporate. It crystallises from a mixture of alcohol and ether in pale-yellow, concentrically-grouped needles melting at 104°. It is insoluble in water, but dissolves readily in ether and benzene, sparingly in alcohol, the solutions showing a blue fluorescence, whereas the solutions in sulphuric and acetic acids have a green fluorescence. Its *picrate*, $C_{21}H_{15}N.C_6H_3N_3O_7$, crystallises in slender, golden-yellow needles which melt at 230°; and the *dichromate*, $(C_{21}H_{15}N)_2,H_2Cr_2O_7$, forms slender, orange-red prisms, insoluble in water. The *platinochloride*, $(C_{21}H_{15}N)_2,H_2PtCl_6$, is a microcrystalline, orange-yellow precipitate, sparingly soluble in water and alcohol.

When α-cinnamenyl-α-naphthacinchonic acid is oxidised in the cold with dilute potassium permanganate solution, the cinnamenyl-group is converted into carboxyl, *α-naphthaquinoline-αγ-dicarboxylic acid*, $COOH{\cdot}C{\Large<}{\begin{matrix}N-C_{10}H_6\\ CH{:}C{\cdot}COOH\end{matrix}}$, being formed. This crystallises from alcohol in greenish-yellow, concentrically-grouped needles which melt at 278° with decomposition, and are soluble in hot alcohol and acetic acid, and in hot concentrated mineral acids. The *silver* salt, $C_{15}H_7NO_4Ag_2$, and the *copper* salt, $C_{15}H_7NO_4Cu + 2H_2O$, are obtained as white and dirty-green precipitates by adding silver nitrate or copper acetate to a solution of the ammonium salt. On distillation, the acid splits up into carbonic anhydride and α-naphthaquinoline, the latter being identical with the compound obtained by Skraup and Cobenzl (Abstr., 1881, 920; 1883, 1010).

When either of the foregoing acids is treated with potassium permanganate at 80—90°, *α-phenylenepyridineketonedicarboxylic acid*, ${\begin{matrix}CO-\\ C_6H_4\end{matrix}}{\Large>}C_5NH(COOH)_2$, is formed, and may be isolated by filtering off the manganese dioxide, concentrating, adding hydrochloric acid, and recrystallising the precipitate from hot water. It forms long, lustrous, yellow needles which melt at 264°, and are sparingly soluble in cold water, ether, and alcohol, readily in hot water and acetic acid; it also dissolves in alkalis with a red colour. The *silver* salt, $C_{14}H_5NO_5Ag_2$, is a voluminous, yellow precipitate.

On distillation, the acid splits up into carbonic anhydride and α-phenylenepyridineketone, the properties of which agree exactly with those given by Skraup and Cobenzl (*loc. cit.*)

α-Cinnamenyl-β-naphthacinchonic acid, $CHPh{:}CH{\cdot}C{\Large<}{\begin{matrix}N-C_{10}H_6\\ CH{:}C{\cdot}COOH\end{matrix}}$,

is prepared in exactly the same manner as the corresponding α-compound, β-naphthylamine being substituted for α-naphthylamine. It forms lustrous, citron-yellow needles melting at 305°, and is insoluble or sparingly soluble in the ordinary solvents, crystallising best from alcohol containing a little hydrochloric acid. The salts of the alkalis and alkaline earths are crystalline compounds, sparingly soluble in cold, more readily in hot water. The *silver* salt, $C_{22}H_{14}NO_2Ag$, is a white, flocculent precipitate.

The acid, like the α-compound, splits up on heating by itself or with soda-lime into *α-cinnamenyl-β-naphthaquinoline*,

$$CHPh{:}CH{\cdot}C{\lessdot}\begin{matrix}N-C_{10}H_6\\ \vert \\ CH{:}CH\end{matrix},$$

and carbonic anhydride. The former crystallises from a mixture of alcohol and ether in white, silky needles melting at 175°, and readily soluble in acetic acid, sparingly in alcohol and acetone, and insoluble in water. The *platinochloride*, $(C_{12}H_{15}N)_2,H_2PtCl_6 + 2H_2O$, forms orange-yellow plates which lose their water of crystallisation at 110°. The *dichromate*, $(C_{21}H_{15}N)_2,H_2Cr_2O_7$, crystallises in yellow needles; and the *picrate*, $C_{21}H_{15}N,C_6H_3N_3O_7$, in golden-yellow needles melting at 254°.

On oxidation with potassium permanganate in the cold, α-cinnamenyl-β-naphthacinchonic acid yields *β-naphthaquinoline-αγ-dicarboxylic acid*, which crystallises in pale-yellow, slender needles melting at 288°, and soluble in acetic acid and hot alcohol. The *barium* salt, $C_{15}H_7NO_4Ba + H_2O$, is a white, flocculent precipitate; and the *silver* salt, $C_{15}H_7NO_4Ag_2$, a white precipitate. On distillation, the acid yields β-naphthaquinoline, which crystallises in white plates, and is identical with Skraup and Cobenzl's compound.

It follows from this that α-cinnamenyl-β-naphthacinchonic acid has the formula analogous to that of phenanthrene previously assigned to it, and has not a formula corresponding with that of anthracene.

By the oxidation of both the foregoing acids with potassium permanganate at 80—90°, *β-phenylenepyridineketonedicarboxylic acid*, $\begin{matrix}CO-\\ \vert \\ C_6H_4\end{matrix}{>}C_5NH(COOH)_2$, is formed. It crystallises from hot water in citron-yellow needles melting at 284°, sparingly soluble in water, alcohol, and ether, readily in acetone and acetic acid. It is very hygroscopic, and is only completely dried at 140°. Its *silver* salt, $C_{14}H_5NO_5Ag_2$, is a white, almost insoluble precipitate. When heated above its melting point, β-phenylenepyridineketonedicarboxylic acid loses carbonic anhydride, and forms a yellowish-brown oil which solidifies on cooling, and crystallises from hot water in colourless needles melting at 128—129°, readily soluble in alcohol. It is a base, and is therefore readily dissolved by acids and reprecipitated by alkalis. The platinochloride, $(C_{12}H_7NO)_2,H_2PtCl_6 + 2H_2O$, forms beautiful, orange-yellow needles which lose their water of crystallisation at 110°.

H. G. C.

Synthesis of Pyrazole. By L. Balbiano (*Ber.*, **23**, 1103—1108).—Epichlorhydrin, dissolved in absolute alcohol, was treated with

hydrazine hydrate and boiled for five hours in a reflux apparatus. On cooling, hydrazine hydrochloride was deposited, and the alcoholic solution left, on evaporation, a yellow syrup easily soluble in water. No definite compound could be isolated from this, but it reduces platinum chloride, and doubtless contains the compound $O<\begin{matrix}CH\cdot CH_2\cdot N_2H_3\\ | \\ CH_2\end{matrix}$.

Hydrazine hydrate was then treated with epichlorhydrin in a reflux apparatus, and when the reaction was over, the mixture was heated for 30 minutes on a water-bath, treated with powdered zinc chloride (to act as a dehydrating agent), and heated for an hour longer. The resinous mass thus obtained was treated with water and distilled in a current of steam, the distillate, which contained pyrazole and ammonia, being collected until it ceased to give a precipitate with mercury chloride. The whole distillate was then treated with mercury chloride, and the mercury compound of pyrazole and ammonia suspended in water and decomposed with hydrogen sulphide. The solution was concentrated, treated with aqueous potash, and extracted with ether. The ether extract left, on evaporation, colourless needles of pyrazole, $C_3N_2H_4$, soluble in water, alcohol, and ether, having a faint odour of pyridine, melting at 69·5—70° and boiling at 186—188° under 757·9 mm. pressure. In all these properties it resembles the substance obtained by Buchner (Abstr., 1888, 1274, and 1889, 694), by heating methyl acetylenedicarboxydiazoacetate. The platinochloride and picrate of these two substances are also identical.

Pyrazole platinochloride, $(C_3N_2H_4)_2,H_2PtCl_6 + 2H_2O$, forms yellowish-red needles soluble in water and alcohol. When heated at 100°, it loses $2H_2O$, and at 200—210°, loses 4HCl besides, forming the compound $(C_3N_2H_3)_2PtCl_2$, which, at a little above 250°, decomposes without melting.

Pyrazole picrate, $C_3N_2H_4.C_6H_2(NO_2)_3\cdot OH$, forms small, yellow needles soluble in alcohol, and slightly in cold water, and melting at 159—160°.

C. F. B.

The Relation between Cocaïne and Atropine. By A. EINHORN (*Ber.*, 23, 1338—1344).—It has already been shown by Ladenburg (Abstr., 1883, 670; 1887, 740; and this vol., p. 67) that the tropine obtained from atropine is a 1-methyl-α-hydroxyethyltetrahydropyridine, the position of the double linkage not having been ascertained. Buchka gives, as the most probable formula,

$$\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot CH_2\cdot CH_2\cdot OH\\ | \qquad\qquad | \\ CH\!:\!CH\cdot NMe\end{matrix}.$$

The tropidine obtained from this by elimination of water would then have the formula $\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot CH\!:\!CH_2\\ | \qquad\qquad | \\ CH\!:\!CH\cdot NMe\end{matrix}$, which is closely connected with the formula proposed by the author for anhydroecgonine, $\begin{matrix}CH_2\cdot CH_2\cdot CH\cdot CH\!:\!CH\cdot COOH\\ | \qquad\qquad | \\ CH\!:\!CH\cdot NMe\end{matrix}$.

By the action of concentrated hydrochloric acid at 280° on anhydroecgonine, the author obtained a mixture of pyridine bases, one of which gave an aurochloride melting at 212°, the base of which appeared to have the formula $C_7H_{13}N$ (Abstr., 1889, 909). A microcrystallographic examination of this salt by Lehmann showed that it contained an impurity. The base was therefore isolated as the *picrate*, which is readily obtained pure by crystallisation from water. From this pure compound, the *aurochloride* and *platinochloride* may be obtained in the pure condition. The numbers found on analysis agree with the formula $C_8H_{13}N$, instead of $C_7H_{13}N$, and the crystallographic examination by Arzruni and Lehmann of the three salts, and the corresponding salts of tropidine, has shown their complete identity. The picrate from both sources forms long crystals with a distinct longitudinal cleavage; the aurochloride exists in two enantiotropic modifications which are converted into one another at a temperature below the boiling point of water. The platinochloride also exists in two modifications, the one of which is rhombic, and the other monoclinic, the former having an orange and the latter a cinnabar-red colour.

These facts show, therefore, the genetic relationships which exist between anhydroecognine and tropidine, and also support the formula given by Buchka for the latter compound. The only step now wanting for the conversion of cocaïne into atropine is the formation of tropine from tropidine by the addition of the elements of water.

H. G. C.

Methylcocaïne. By F. Giesel (*Chem. Centr.*, 1890, i. 718—719; from *Pharm. Zeit.*, **35**, 137—138).—The author has isolated a well characterised base from the mother liquors obtained in the preparation of cocaïne from ecgonine. It is very readily soluble in ether, and separates from this solvent as an oil, which becomes solid and crystalline at a low temperature. It melts at 40°. Its salts are generally somewhat less soluble than those of cocaïne. The nitrate especially, and also the sulphate and hydrobromide, may be used to separate the new base from cocaïne. With potassium permanganate, chromic acid, and gold chloride. it behaves as cocaïne does. When heated with hydrochloric acid, benzoic acid and methylecgonine were obtained in quantities corresponding with the formula of *methylcocaïne*, $C_{18}H_{23}NO_4$. In the hydrolysis by hydrochloric acid, benzoylmethylecgonine hydrochloride is obtained as a middle product. Benzoylmethylecgonine differs from ecgonine and anhydroecgonine in being almost insoluble in absolute ethyl and methyl alcohols.

J. W. L.

Berberine and Hydroberberine. By R. Gaze (*Chem. Centr.*, 1890, i, 590—591; from *Zeit. Naturwiss. Halle*, **62**, 399—457).—The author prepares pure berberine from *acetoneberberine*,

$$C_{20}H_{17}NO_4,C_3H_6O,$$

which is prepared from berberine sulphate. 50 grams of berberine sulphate is treated with 1000 grams of water and 500 grams of acetone, with addition of sodium hydroxide. The acetoneberberine is

decomposed by heating with chloroform and alcohol for 12 hours. The pure berberine salts may be prepared from acetoneberberine by heating it with the acid until completely dissolved. Berberine, as prepared by the author, contains $5\frac{1}{2}$ or 6 mols. H_2O. The compound with 6 mols. is stable in the air, but if heated or if placed over concentrated sulphuric acid for some time, 4 mols. of water are liberated, and the alkaloïd now absorbs water and carbonic anhydride with avidity.

Tetrabromoberberine hydrobromide, $C_{20}H_{17}NO_4Br_4,HBr$, prepared by the action of excess of bromine on the aqueous solution of berberine sulphate, forms dark red crystals. Cold alcohol causes a loss of 2 atoms of bromine, and by warming with alcohol the 4 atoms are abstracted, the hydrobromide remaining.

Bromoform unites with freshly precipitated berberine forming *bromoformberberine*, a somewhat unstable compound, being resolved into the hydrobromide by solution in acetone or benzene, and converted into *chloroformberberine* by solution in chloroform; the latter melts at 178—179°.

A sulphide, probably the pentasulphide, is formed by the action of yellow ammonium sulphide.

Hydroberberine, $C_{20}H_{21}NO_4$, first prepared by Hlasiwitz and Gilm by the action of sulphuric acid (15 c.c.), glacial acetic acid (20 c.c.), and water (200 c.c.) on berberine sulphate (8 grams), has been examined by the author regarding the following reactions: (*a*) with methyl iodide, the methiodide, $C_{20}H_{21}NO_4,MeI + H_2O$, which forms white crystals melting at 228—235°, is formed. (*b*) The chloride, $C_{20}H_{21}NO_4,MeCl + 3H_2O$, is obtained from the last named by the action of silver chloride. (*c*) the hydroxide, $C_{20}H_{21}NO_4,MeOH + 3\frac{1}{2}H_2O$ (?), which melts at 162—164°, and is unstable and crystalline, is prepared from the iodide by means of moist silver oxide. When heated in a current of hydrogen, the methyl-group becomes combined in the berberine molecule, forming *methylhydroberberine*, $C_{21}H_{23}NO_4 + 2H_2O$, which forms colourless needles melting at 224—226°. (*d*) *Hydroberberine ethiodide*, $C_{20}H_{21}NO_4EtI + H_2O$, melts at 223—225°. (*e*) *Hydroberberine ethochloride* contains $2\frac{1}{2}$ mols. of water, and melts at 138—140° in its water of crystallisation, and at 225° when anhydrous. (*f*) *Ethylammonium base*, $C_{20}H_{21}NO_4,EtOH + 4H_2O$, melts at 158—161°, and forms colourless crystals, which are exceedingly bitter; from this, *ethylhydroberberine*, $C_{22}H_{25}NO_4 + 4\frac{1}{2}H_2O$, is obtained, which melts at 233—235°, forms colourless crystals, and does not behave as a tertiary base. Bromine forms an unstable perbromide with hydroberberine.

J. W. L.

Stability of Oxyhæmoglobin. By G. YEO (*Proc. Physiol. Soc.*, 1890, 7).—Tubes were filled with much diluted blood and sealed, the whole of the operations being performed with antiseptic precautions. Six years later, the bands characteristic of oxyhæmoglobin were still visible in most of the tubes (compare this vol., p. 651).

W. D. H.

Methæmoglobin and Sulphur-methæmoglobin. By T. ARAKI (*Zeit. physiol. Chem.*, **14**, 405—415).—The typical absorption band of

methæmoglobin is between the C and D lines of the solar spectrum; two other bands are also described, situated approximately in the positions of the α- and β-bands of oxyhæmoglobin. Many writers regard these bands as due to methæmoglobin itself; the author, however, considers that they are due to admixture with oxyhæmoglobin, because their intensity does not necessarily vary with the concentration of the solution, as the typical band in the red does. On treating solutions of carbonic oxide-hæmoglobin with potassium ferricyanide, methæmoglobin is formed slowly.

Experiments were performed in order to see what happens when a solution of methæmoglobin is allowed to undergo putrefaction in a sealed tube; the following were the results obtained:—At first, methæmoglobin disappears, and the bands of oxyhæmoglobin, then that of hæmoglobin appears; by shaking the latter with the air, oxyhæmoglobin is again formed.

Sulphur-methæmoglobin is the substance which gives the greenish hue to dead bodies during putrefactive processes; it was originally described by Hoppe-Seyler (*Med. Centr.*, 1863, No. 28). It can be obtained from blood by passing oxygen and hydrogen sulphide through it. The lines of the solar spectrum coincided with the following numbers on the scale used; C = 46; D = 80; E = 125; b = 134; F = 165. The absorption-bands of an aqueous solution of sulphur-methæmoglobin were as follows: Ia = 45—55, ill-defined; Ib = 60—68, dark and well marked; the space 55—60 was shaded. On shaking this solution with the air, oxyhæmoglobin was formed; by the action of sodium hydroxide, hæmochromogen makes its appearance; the group of atoms which is present as hæmochromogen in hæmoglobin is thus also present as such in sulphur-methæmoglobin. All attempts to obtain sulphur-methæmoglobin in a crystalline form, or to obtain hæmin crystals from it, or to obtain a sulphur containing hæmatin from it, failed. W. D. H.

Physiological Chemistry.

Decomposition of Ethereal Salts in the Alimentary Canal. By H. K. L. Baas (*Zeit. physiol. Chem.*, **14**, 416—436).—Researches on the digestion of fats have shown that these substances undergo only a small amount of decomposition in the intestine, and theories have been formulated to explain how this assists the absorption of the emulsified fats. It was thought that some light might be thrown on the subject by investigating simpler substances having a similar constitution to the fats. The drugs were taken by the experimenter himself, or administered to dogs, and the urine and fæces subsequently examined, in order to see how much of the material taken had undergone decomposition. The following example of an experiment will serve as an illustration of the methods adopted and results obtained.

This experiment (on a dog) lasted seven days; on the fourth day, 5 grams of methyl salicylate was given; the following table gives analytical details regarding the urine:—

Day.	Total excretion of sulphates.		B : A.
	A. Normal sulphates.	B. Ethereal hydrogen sulphates.	
1..........	0·4052	0·0628	1 : 6·48
2..........	0·4548	0·0802	1 : 5·67
3..........	0·2264	0·0394	1 : 5·75
4..........	0·1204	0·0245	1 : 4·92
5..........	0·8202	0·4195	1 : 1·95
6..........	0·3468	0·1017	1 : 3·43
7..........	0·1804	0·0290	1 : 6·22

From the first to the fourth day, the daily average of ethereal hydrogen sulphates was 0·0513. The increase of these on the fifth and sixth days corresponds with 12·98 per cent. of the drug given. The amount of salicyluric acid in the urine of the fifth, sixth, and seventh days was 1·517 gram; adding this to the increase of ethereal hydrogen sulphates, it is calculated that 23·68 per cent. of the drug is accounted for, and, therefore, that amount probably underwent decomposition in the body. Another drug investigated was salol (phenyl salicylate); it was much more fully decomposed (from 43 to 69 per cent.), and this produced much greater toxic effects than the first mentioned.

The following table gives the mean results obtained in this, and previous researches of the same nature:—

Drug.	Amount of decomposition in the body.	
Glyceryl benzoate ..	54, 61·6, and 97 per cent.	Schmiedeberg (*Arch. exp. Path. u. Pharmak.*, **16**, 367).
Phenyl succinate....	84 per cent.............	
Phenyl benzoate	Complete..............	
Phenyl carbonate ...	68·33 per cent. (Lesnik, *ibid.*, **24**, 167).	
Phenyl salicylate (salol)	43·95 and 69·06 per cent.	Present research.
Ethyl salicylate.....	21·21 per cent.	
Methyl salicylate ...	23·66 and 24·75 per cent.	
Neutral fats........	Very slight (Cl. Bernard, Maly, Munk)	

The present research shows that only a comparatively small amount of the drug given undergoes decomposition. W. D. H.

Proteïds of Liver and Kidney Cells. By W. D. HALLIBURTON (*Proc. Physiol. Soc.*, 1890, 7).—The proteïds obtainable from liver and kidney cells belong almost exclusively to the class of globulins. The nucleo-albumin, which was previously described in lymph cells (Abstr., 1888, 974), is absent from liver cells, but present in kidney

cells. No evidence of true myosin or myosinogen is found in either. Although portions of the fresh tissues are found to hasten the coagulation of salted blood-plasma, and of hydrocele and pericardial fluids very considerably, this power is destroyed at a fairly low temperature, and all attempts to prepare fibrin-ferment from the cells by Schmidt's alcohol method failed. W. D. H.

The Proportion of Blood to Body Weight. By S. M. COPEMAN and C. S. SHERRINGTON (*Proc. Physiol. Soc.*, 1890, 8—9).—The method employed for determining the proportion of the weight of the blood to that of the whole body is one which can be readily performed on the living animal, and may be best described by an example:—A rabbit was anæsthetised with chloral and chloroform, and the right cervical sympathetic was divided; a drop of arterial blood taken from the right ear was then ascertained, by the method of Roy (Abstr., 1887, 608), to be of a certain specific gravity (in this experiment 1·0520); 30 c.c. of 0·75 sodium chloride solution having a specific gravity of 1·0046 at a temperature of 38° was then injected into the external jugular vein in 15 seconds. 30 seconds later, a drop of arterial blood was again taken from the right ear, and the sp. gr. of it estimated as before (found in this experiment to be 1·0470). The weight of the animal before the injection was 3572 grams; no solid food had been given for 30 hours before the experiment. On two assumptions, (i) that the blood and injected fluid were thoroughly mixed together in the 30 to 45 seconds; and (ii) that only a negligible quantity had escaped from the circulation in that time, the calculation ran as follows:—

$$30.\ 1{\cdot}0046 + 1{\cdot}0520 = (30 + x)\ 1{\cdot}0470,$$
$$x = 254{\cdot}4 \text{ c.c. weighing } 267{\cdot}6 \text{ grams.}$$
$$\frac{267{\cdot}6}{3572} = 7{\cdot}49 \text{ p. c. of body weight.}$$

It is urged that the method gives results which are, at least, trustworthy for comparison one with another. Working with it, it was found that young animals possess relatively to body weight a larger quantity of blood than adult animals, and that in a period of abstention from food, water being allowed, the amount of blood relatively to the body weight increases very largely.

Experiments on dilution of the circulating blood were also performed. 30 c.c. of saline solution injected quickly, namely, in 20 seconds *per venam*, appears to become thoroughly mixed with the circulating blood in 30 to 45 seconds. Physiological saline solution thrown into the circulation is removed from it with very great rapidity, for instance, 30 c.c. injected into the circulation of the rabbit may almost completely disappear from it in 10 minutes' time. This immediate disappearance does not take place to any great extent by the kidneys—the rate of removal not being appreciably less rapid after taking the kidneys out of the circulation. The rate of removal is hardly appreciably altered by cutting the limbs out of the circulation, nor by section of the spinal cord behind the bulb. By con-

tinuous injection of "normal" saline solution, the sp. gr. of the blood may be kept for an hour at 1·030, the normal being 1·055, without production of any obvious signs of distress; naturally, the urinary and other secretions become greatly increased, and of a watery character. Hæmorrhage causes a fall in the sp. gr. of the blood, reaching its lowest 20—30 minutes after the hæmorrhage. Division of the spinal cord behind the bulb also causes a fall in the sp. gr. of the blood; this fall is slight, and reaches its full extent almost immediately. By injection of a strong solution of sugar or sodium chloride, the sp. gr. of the circulating blood may in a few minutes be lowered by 20 degrees. 100 c.c. of water placed in the peritoneal cavity of a rabbit may disappear from it completely in eight hours without a lowering of sp. gr. of the circulating blood, except to the extent of half a degree for a varying number of minutes immediately after the placing of the fluid in the peritoneal cavity; the water is, however, during the eight hours largely, if not entirely, got rid of in the urinary and intestinal secretions. The sp. gr. of blood from the jugular had on many occasions been compared with that from the carotid, but had never been observed to differ from it by more than so slight an extent as to leave the matter dubious. On the other hand, the blood of the splenic vein had on several occasions been found to be of a higher sp. gr. than the arterial blood; also on several, but fewer, occasions, the blood of the renal vein had been found to be of lower sp. gr. than the arterial blood (compare this vol., p. 808). In an area in which there is obstruction to the circulation from the venous side, the blood rapidly becomes of high sp. gr., and may be found 20 degrees higher than before the obstruction. A very constant effect of operative interference with the peritoneal cavity is a heightening of the sp. gr. of the circulating blood; the mere opening of the peritoneal cavity through the linea alba may be followed by an increase of the sp. gr. of the blood to the extent of six or seven degrees, this increase reaching its maximum a variable number of hours after the operation (compare this vol., p. 393). Abstention from food, except water, at first causes a diminution in the sp. gr. of the blood; later, the sp. gr. of the blood increases, and becomes in time considerably above its normal as observed before the commencement of the period of abstention. W. D. H.

Is Free Hæmoglobin present in the Blood-plasma of the Splenic Vein? By E. A. Schäfer (*Proc. Physiol. Soc.*, 1890, 9—10). —The observations were made for the purpose of testing the statement which occurs in many text-books of physiology (the origin of which appears to be obscure) that the blood-plasma of the splenic vein normally contains free hæmoglobin. The method adopted was to allow the blood to flow directly from the vein into a carefully cleaned and previously superheated glass tube, within which it was allowed to coagulate, and, after the shrinking and subsidence of the clot, the serum was then examined with the spectroscope. In every case a control tube of arterial blood of the same animal was taken at the same time. The blood of a large number of animals of different kinds (rabbit, cat, dog, monkey), killed at various stages of digestion,

has been in this way examined in the course of the last two years, with the result of proving that free hæmoglobin is normally absent both in the blood-plasma of the splenic vein and in that of arterial blood. In some of the experiments, the serum from both sources was found to be slightly coloured with free hæmoglobin, but not more so in the case of that derived from the blood of the splenic vein than in that derived from the general arterial blood; indeed, there was sometimes a preponderance in favour of the arterial serum. The opinion is held that such coloration is not normal, but is due to the setting free of some of the hæmoglobin by a destruction of red corpuscles resulting from an accidental cause, which in these experiments was probably to be looked for in the chloroform or ether which had been administered as an anæsthetic. W. D. H.

Lecithin and Cholesterin in Red Blood Corpuscles. By P. MANASSE (*Zeit. physiol. Chem.*, **14**, 437—452).—The cholesterin in the red corpuscles of the blood is identical with that obtained from gall-stones, in melting point, specific rotatory power, and reactions. The rotatory power in chloroform solutions sinks with a rise of temperature. The corpuscles contain as a mean 0·151 per cent. of cholesterin. The lecithin of the red corpuscles is similarly identical with that obtained from egg-yolk, brain, &c. The decomposition-products are in all cases the same. The corpuscles contain as a mean 1·867 per cent. of lecithin. W. D. H.

Pernicious Anæmia. By W. HUNTER (*Brit. Med. Journ.*, 1890, ii, 1—4, 81—85).—A case of this disease is described with clinical details. The urine was normal in quantity, of low specific gravity, and contained as its principal pigment "pathological urobilin" (compare this vol., p. 400). Occasionally cells of renal origin containing blood-pigment were present. The urine contained excess of iron; the average secretion of iron in the urine in health is from 3 to 5 milligrams daily; in three cases of chlorosis it averaged 1·76 milligrams; in the present case it varied from 6·5 to 32·3 milligrams. The liver was found to be richer in iron than normal.

The opinion was formerly expressed (Abstr., 1888, 1324) that the destruction of the blood corpuscles, characteristic of the disease, which occurs in the portal circulation, and which is similar in essential characteristics to that produced by poisoning with toluylenediamine, is probably brought about by certain poisonous agents of a cadaveric nature absorbed from the intestinal tract. Special attention was therefore directed to the products of putrefaction in the urine. Estimation of the ethereal hydrogen sulphates and their ratio to the normal sulphates showed that the absolute amount of putrefaction as measured by that of the aromatic sulphates was not increased; the normal ratio of the two classes of sulphates was, however, considerably altered, being 1 : 3 instead of the normal 1 : 10. Improvements in the patients' condition were coincident with returns to the normal ratio.

It was further found that the urine contained a ptomaïne, putrescine (tetramethylenediamine), a substance absent in the urine of

health, and that of most diseased conditions, but present in that of cystinuria, and probably also in that of cases of cholera (see Baumann and Udránszky, Abstr., 1889, 1024). In one specimen another diamine which was not fully identified was also discovered. These diamines are not, however, markedly toxic, and they can hardly be considered the poisons that produce the blood-destruction, but their presence indicates the existence of certain special micro-organisms in the alimentary tract, and, therefore, a condition more than any other favourable to the production of other and more poisonous alkaloïds not yet discovered.

A further support to the supposition that the alimentary tract is the seat of the formation of the poison was found in the fact that the gastro-intestinal mucous membrane was distinctly unhealthy in appearance, showing well-defined patches of inflammation resembling those frequently seen in the kidney when that organ is the seat of localised infection with pathogenic microbes. The neighbouring lymphatic glands were similarly affected. W. D. H.

Cystin in the Urine. By S. Delépine (*Proc. Roy. Soc.*, **47**, 198).—The examination of several specimens of urine from which cystin was deposited led to the following conclusions:—

1. That the simple addition of an acid in which cystin is not soluble is not sufficient to separate cystin from the urine, and therefore that the theory generally held as to the state of combination of cystin in the urine is probably inaccurate.
2. That a compound exists in certain urines which under the influence of a fermentation yields cystin.
3. That the fermentation is due to the growth of an organism which can seemingly be separated from the urine by ordinary filtration, and must therefore be a large organism, possibly a torula.
4. That the cases recorded in which cystin has been found deposited in the kidneys and liver indicate that the fermentation may begin in the organism. W. D. H.

Action of Related Chemical Compounds on Animals. By W. Gibbs and H. A. Hare (*Amer. Chem. J.*, **12**, 365—379; compare this vol., pp. 280 and 813).—*The Toluidines.*—Orthotoluidine, both in the frog and in the dog, produces decreased reflex activity and power, followed by an increase in both these functions, and finally by another decrease, deepening into paralysis, coma, and death. It has but little effect on the heart, except by direct contact when in large amount, but it causes a breaking down of the blood with formation of methæmoglobin, and a depression of the spinal cord. In the warm-blooded animal it produces a marked fall of temperature equal to 4° or 5°. Death is produced by respiratory failure, and eventually the heart stops in diastole. The pulse is slowed through depression of the heart-muscle, not through stimulation of the pneumogastric nerves. The vaso-motor system is also depressed. Metatoluidine changes the blood into methæmoglobin, and produces a loss of reflex activity due to depression of the spinal cord. It lowers the body temperature very remarkably, but only affects the circulation when administered in

large doses. It kills chiefly by respiratory failure, except when sent *en masse* into the heart, when it kills by simultaneous respiratory and cardiac failure. Paratoluidine, like the ortho-compound, produces depression, followed by temporary increase and final loss of reflex activity. Its dominant action is also destruction of the blood corpuscles and formation of methæmoglobin. It depresses the spinal cord, and kills by respiratory failure, the heart beating for some moments afterwards. Under its influence, it is found that in the case of the frog's heart the auricle beats twice to a single beat of the ventricle. When brought, in large amount, into direct contact with the heart, it arrests this viscus in diastole. In small doses of 0·031 gram per kilo., it causes an increase of pulse-rate, which is not due to vagal depression. The lethal dose when injected into the jugular vein is 0·208 gram of ortho-, 0·125 gram of meta-, and 0·10 gram of para-toluidine per kilo. of body weight, but it varies greatly with the rapidity of injection.

The Dihydric Phenols.—Catechol causes epileptic convulsions, accompanied by a slowing of the pulse, due to vagal stimulation, and a fall of blood-pressure; death ensues from respiratory failure, the heart continuing to beat for a few moments later. The blood is also changed in appearance. Resorcinol causes epileptic convulsions with a fall of blood-pressure, due to its action on the vaso-motor system, and a slowing of the pulse, due, at least in part, to peripheral vagal stimulation. The heart is not depressed, and death ensues from respiratory failure, probably from the action of the blood. Quinol causes convulsions accompanied by a fall of blood pressure, due to a slowing of the pulse, or in the case of a larger dose by a rise of blood-pressure, due to increased force of the heart beat. The pulse is at first slowed by stimulation of the vagus, and then becomes very rapid, owing to peripheral pneumogastric palsy. The appearance of the blood is also much changed. The lethal dose is of catechol 0·04 to 0·05 gram, of resorcinol 0·7 to 1·0 gram of quinol 0·08 to 0·1 gram per kilo. of body weight, injected into the jugular vein.

Trihydric Phenols.—Phloroglucinol and Pyrogallol.—Both these substances slow the pulse by vagal stimulation, both change the appearance of the blood, and both kill by vagal stimulation, direct or indirect. The lethal dose is of phloroglucinol 1·0 to 1·2 gram, of pyrogallol 0·08 to 0·1 gram per kilo. of body weight, injected into the jugular vein. C. F. B.

Physiological Action of Hyoscine Hydrochloride. By PAVLOFF (*St. Petersburg Med.-chi. Acad. Dissertations*, No. 9, 1889—90).—From observations on warm-blooded animals with doses varying from 0·00005 gram to 0·02 gram. per kilo. of body weight, it was found that the beat is first slowed from stimulation of the inhibitory apparatus. It is then quickened from a paralysing action on the peripheral inhibitory apparatus. The blood pressure is increased by stimulation of the vaso-motor apparatus, especially the centres in the brain and spinal cord. The respiratory centre is stimulated to a slight extent by large doses. The salivary secretion is diminished. The temperature is not altered. The acidification of the blood is

not hastened. The irritability of the brain is diminished. The sense of touch is not affected, although the perception of pain is somewhat diminished. The pupils are quickly, markedly, and persistently dilated from stimulation of the sympathetic nerves. The pharmacological action is very similar to that of atropine, but the latter does not lower the irritability of the brain cortex. T. M.

Chemistry of Vegetable Physiology and Agriculture.

The Fungus-symbiosis of the Leguminosæ. By B. FRANK (*Tagebl. Versamml. deut. Naturforsch. Aertzte*, 1889, 257—259).—In the first part of the paper, the conditions and mode of formation of nodules on the roots of peas, lupins, and beans are discussed. In the infected plants not only the root nodules, but the above-ground organs (stems, leaf-stalks, &c.) of the plants are found to contain bacteroïds. The roots of *Phaseolus vulgaris* always have nodules containing bacteroïds, even in a sterilised soil. With regard to the physiological meaning of the symbiosis, the author considers that Hellriegel was premature in maintaining that the bacteria of the root nodules bring free nitrogen into combination, and so make it available to the plant, and gives the following reasons:—When peas and lupins are grown in ignited sand containing mineral but no nitrogenous nutriment, an extraordinary difference is shown, according to whether a small amount of a fertile soil is added or not. It is true that the sand contains no nitrogen, but, at the same time, all the organic constituents of an ordinary soil are also wanting. The difference brought about by the infection consists in a whole series of phenomena, resulting in the strengthening of the whole plant. If the non-infected sand is manured with nitrate, there is practically no result with lupins, and very little with peas, indicating that it is not the want of nitrogen which is overcome by the symbiosis. The fertilising action of the rhizoplasmidium is further seen in (1) the increase of total produce, (2) the increased chlorophyll-production, (3) the more energetic carbon-assimilation, (4) the formation of nodules rich in albuminoïds, (5) the increased production of flower, fruit, and seed, and of carbonaceous and nitrogenous vegetable substance. In the case of peas and lupins, this increased production will also take place in soil containing humus but free from organisms, and therefore without nodule-formation; the plants develop even better in a sterilised than in a non-sterilised soil.

With regard to *Phaseolus vulgaris*, the plants will not thrive in a soil free from nitrogen, whether infected or not, but develop well in soil containing humus. N. H. M.

The Rôle of Sugar and its Development during the Growth of the Beetroot. By E. DURIN (*Bied. Centr.*, **19**, 337—338).—The

disappearance of sugar from the beetroot during the second period of its growth is not due to seed formation alone; a considerable portion is used up in developing other organs. A bed of beetroot at the period of ripeness was divided into two equal parts, the one part being left exposed to light and the other kept dark. The plants kept in the dark lost their green leaves and formed a crown of yellow leaves. At the commencement of the experiments the sap of the roots contained 6·95 per cent. of sugar. After eight weeks, the sap of those plants which were kept in the dark contained 3·15 per cent. of sugar, so that half the sugar had been used up in forming new leaves. The rest of the plants were then kept covered, and remained healthy until the percentage of sugar sank to about 0·5—0·6, when they showed a mark which spread quickly until the whole root was rotten. Other experiments were made, the results of which also show that sugar is taken up from the roots to form stalks and leaves, and that the root dies when all the sugar is used up. N. H. M.

Assimilation of Carbon by Green Plants from certain Organic Compounds. By E. H. Acton (*Proc. Roy. Soc.*, **47**, 150—175).—A. Meyer (*Botan. Zeitung* for 1886, pp. 81, 105, 129, 145) found that starch was formed by leaves placed in solutions of various organic substances. The author has extended this investigation, both by using a greater variety of solutions and by supplying them not only directly to the leaves, but also through the medium of the roots. He operated in all on 15 different species, some of which were water plants. His principal experimental results are as follows:—

Starch is formed when the following substances are supplied either to the leaves or to the roots: glucose, cane-sugar, inulin, glycerol.

Starch is formed when soluble starch is supplied to the leaves, but not when it is supplied to the roots.

Humus extract, obtained by digesting leaf-mould with dilute alcohol and filtering, forms starch when supplied to the roots, but not when given directly to the leaves.

Starch is not formed under any circumstances with acraldehyde (and compounds), allyl alcohol, dextrin, glycogen, acetaldehyde (and compounds), levulinic acid, artificial humus from cane-sugar.

Glucose is more readily taken up by roots than cane-sugar, and may all be withdrawn from a 1 per cent. solution.

Many green plants (? all) behave in the same manner to the above substances. J. W.

Presence and Behaviour of Nitric Acid in Plants. By Serno (*Chem. Centr.*, 1890, i, 592—593; from *Landw. Jahrb.*, **18**, 877—905). —The author has examined a large number of plants for nitric acid, and has found it present in nearly all. In some it is present in much larger quantity than in others. Among those in which it exists in almost all the organs are the *Malvaceæ*, *Cruciferæ*, *Papaveraceæ*, *Convolvulaceæ*, *Labiatæ*, *Compositæ*, and the *Urticaceæ*. In others, nitrates were not present in those parts above ground, but were present in the youngest rootlets. It appears to pass from the roots, which absorb it

from the earth, upwards, and becomes used for the formation of the nitrogenous constituents.

In wood-forming plants, the author has found an accumulation of nitrates in the first year until the formation of wood has ceased, and in later periods it is present in the roots, also in the young shoots of early spring. It disappears during the winter. In the case of perennial herbs also, nitric acid was found in the newly-formed fibrous roots; during the winter they store it up for transformation in spring, when the new growth commences. In the case of cultures in distilled water, asparagine disappeared during the later stages of growth, but was formed again as soon as nitrates were added. The author considers this a proof that nitric acid is transformed into amido-compounds, especially asparagine. J. W. L.

Carbohydrates in Peach Gum. By W. E. Stone (*Amer. Chem. J.*, **12**, 435—440).—The gum which exudes from the bark of the wild peach-tree when it is injured, or from the fruit when punctured by insects, was heated with dilute sulphuric acid for 10 hours, the solution then neutralised with barium carbonate, filtered, and evaporated. The syrup thus obtained was boiled with alcohol, and the clear alcoholic solution decanted and evaporated. A white, crystalline substance was then obtained, which, by fractional crystallisation, followed by repeated recrystallisation of the fractions, was resolved into two compounds having specific rotatory powers equivalent respectively to those of arabinose and galactose. That one of these is arabinose was shown by the melting point of its phenylhydrazine compound, and by its yielding furfuramide when it is distilled with sulphuric acid, and the distillate treated with ammonia. The other, from the melting point of its phenylhydrazine compounds, and from its yielding mucic acid when oxidised with nitric acid, was identified as galactose. Peach gum, therefore, contains both arabinose and galactose, that is, a true glucose associated with a pentaglucose.

C. F. B.

Carbohydrates of the Sweet Potato (Batatas edulis). By W. E. Stone (*Ber.*, **23**, 1406—1408).—Finely-divided sweet potatoes were boiled for some time with strong alcohol; after filtering and concentrating the solution, cane-sugar crystallised out. It was identified by its specific rotatory power, its fermentability with yeast, and its behaviour towards Fehling's solution both before and after hydrolysis. The quantity of sugar in the potatoes was found to be $1\frac{1}{2}$—2 per cent. Baking the potatoes converted part of the starch into the soluble form, and caused the cane-sugar to be hydrolysed to glucose. J. B. T.

Experiments with Beetroot. By O. Kohlrausch and F. Strohmer (*Bied. Centr.*, **19**, 322—333).—The results of previous experiments indicated that no increase in the amount of sugar in beetroot is obtained by increased manuring with potassium nitrate, and that the physiological actions of the potash and the nitric acid partly cancel each other in the production of sugar. The authors have repeated the experiments in the same place and under the same

conditions, manuring with sodium nitrate and potassium phosphate in order to determine whether the low amount of sugar was due to the potassium nitrate or to local conditions. The experiments were conducted in vessels containing 25 kilos. of sand, and seeds of a uniform size were employed.

The following conclusions are drawn from the results of the experiments extending over five years:—(1) The application of increasing amounts of potash gives rise to a corresponding increased production of sugar. (2) An increased manuring with nitric acid has the effect of increasing the amount of leaf of the plants, and is unfavourable to sugar-formation, so that the production of sugar is diminished. (3) The increased nitric acid manuring has also the effect of raising the amount of nitric acid, and also the proteïn in the roots. (4) The increased sugar production brought about by the application of potash is at once cancelled by the physiological action of the corresponding amount of nitric acid. (5) Phosphoric acid influences leaf growth in a manner favourable to sugar production, and expedites the ripening of the plants; phosphoric acid, therefore, assists the favourable action of potash in the formation of sugar.

N. H. M.

Source of Nitrogen of Plants. By A. G. SCHMITTER (*Bied. Centr.*, 1890, 393—395).—The growth of lupins on poor moorland soils was compared with the growth on the same soils improved by the addition of fertile soil. No perceptible difference was noticed in the growths of the two sets of plants; at any rate the difference was so slight, as to render useless the extra expense, &c., occasioned by the addition of fertile earth.

E. W. P.

Loss and Gain of Nitrogen by Soil. By A. PAGNOUL (*Compt. rend.*, **110**, 910—912).—The experiments were carried out in pots which contained 22 kilos. of earth each, the surface exposed being 7·54 square decimetres, and the pots being so constructed that the water could readily drain away. The 22 kilos. contained 22·44 grams of nitrogen, and to this was added 0·540 gram in the form of dried blood, and 1·0 gram in the form of ammonium sulphate, giving a total of 23·980 grams of nitrogen in the 22 kilos. of soil. Two lots, A and *a*, were left without any crop, two, B and *b*, were sown with grass, and two, C and *c*, with clover. After a year (March, 1888 to March 1889), the following results were obtained:—

	A.	*a.*	B.	*b.*	C.	*c.*
Nitrogen remaining in the soil	24·640	23·760	26·180	27·720	29·260	32·340
Nitrogen removed in the crops	—	—	1·490	1·456	4·266	4·144
Nitrogen in the drainage water	0·967	0·779	0·071	0·088	0·212	0·184
Total	25·607	24·539	27·741	29·264	33·738	36·668
Nitrogen gained from the air	1·607	0·559	3·761	5·284	9·758	12·688

The gain of nitrogen per hectare *by the soil* is as follows:—(1) no crop, 29 kilos.; (2) grass, 394 kilos.; (3) clover, 904 kilos.

The proportion of ammoniacal and nitric nitrogen removed by the drainage water in each case was as follows:—

	No crop.		Grass.		Clover.	
Ammoniacal nitrogen	0·025	0·017	0·024	0·020	0·021	0·016
Nitric nitrogen	0·942	0·762	0·047	0·068	0·191	0·168

C. H. B.

Analytical Chemistry.

Ruffle's Method of Estimating Ammonia. By A. BUCHAN (*Chem. News*, **61**, 231).—To prevent fusion of the contents of the tube in estimating ammonia, the author prepares his soda-lime by heating a mixture of equal proportions of ground quick-lime and sodium carbonate until all aqueous vapour is eliminated.

D. A. L.

Estimation of Ammonia in Sand and Sewage. By A. HAZEN (*Amer. Chem. J.*, **12**, 427—428).—The sand (from filters) is placed in a small flask fitted with two tubes, one of which passes to the bottom of the flask, whilst the other is connected to a condenser. Through the first, steam, obtained by boiling water previously freed from ammonia, is blown in until 50 c.c. of distillate has been collected; this, it is found, contains all the free ammonia in the sand. Alkaline permanganate of full strength is then placed in the flask, and the distillation continued; the first 50 c.c. of distillate contains eight- or nine-tenths of the albuminoïd ammonia, and the rest comes over with the next 50 c.c. The flask may, if necessary, be heated with a small flame. The process is also well adapted to the examination of sewage, and anything that contains enough ammonia. It takes less time than the ordinary method, and gives the same results for free ammonia, but somewhat higher for albuminoïd ammonia; but in the latter case the results are sharper, and different experiments agree better. The author prefers the use of indiarubber, freed from ammonia by long boiling, for stoppers and connections. C. F. B.

Effect of Temperature on the Nessler Test. By A. HAZEN and H. W. CLARK (*Amer. Chem. J.*, **12**, 425—426).—The authors find that the low results obtained by them and by Smart were due, not to imperfect condensation of the ammonia, but to the low temperature of the distillates, which had been condensed in a block-tin condenser. It is found that the colour produced in the Nessler test varies with the temperature, and is deeper according as the solution is warmer; it is thus necessary to bring the distillate and the standard ammonia solution to the same temperature before comparing the tints which they give with the Nessler solution. C. F. B.

Estimation of Nitric Acid by Reduction to Ammonia. By E. Boyer (*Compt. rend.*, **110**, 954—956).—The reduction of nitric acid to ammonia by the action of zinc and hydrochloric acid is generally incomplete, oxides of nitrogen, and even free nitrogen, being evolved. By careful attention to the conditions, however, the reduction can be made complete, and can be utilised for the estimation of nitric acid.

5 grams of zinc, in granules the size of peas, is introduced into a test-tube 300 mm. long and 22 mm. in diameter; 10 c.c. of the solution containing not more than 0·5 gram of the nitrate is then added, and 5 c.c. of hydrochloric acid of sp. gr. not lower than 1·19. When the evolution of hydrogen ceases, a further quantity of 5 c.c. of acid is added, and the reduction is complete in 10 minutes. Success depends on careful attention to the concentration and proportions of the solutions.

The ammonia is estimated in the usual way, but must be expelled by means of magnesia, since sodium or potassium hydroxide forms an insoluble ammonia-derivative in presence of zinc. The liquid is mixed with potash or soda until just alkaline and about 2 grams of magnesia is added. C. H. B.

Estimation of Nitric Acid by Schulze and Tiemann's Method. By L. Spiegel (*Ber.*, **23**, 1361—1363).—The author has previously shown (*Zeitsch. für Hygiene*, 1887, 163) that in Schulze and Tiemann's method of estimating nitric acid in drinking water, an error of at least 3 per cent. occurs, unless the gases in the decomposition flask are driven out at the end of the operation by carbonic anhydride. In reply to the objection of Tiemann that carbonic anhydride is difficult to obtain free from air, the author states that if the pieces of marble are allowed to remain in warm water before being placed in Kipp's apparatus, the gas evolved is practically free from air in half an hour.

The following apparatus, in which the necessity of creating a vacuum is avoided, is described by the author as the most suitable. An ordinary bolt-head of about 150 c.c. capacity is fitted with a doubly-bored caoutchouc stopper, through which are passed entrance and exit tubes. The latter reaches to within 2 c.c. of the bottom, and has blown on it, above the cork, a bulb of about 50 c.c. capacity. Into the tube at the lower end of the bulb a second tube is ground, which is connected with the apparatus evolving carbonic anhydride.

After the water has been placed in the flask, carbonic anhydride is passed through the apparatus until all the air has been driven out, and about 20 c.c. of freshly prepared and well-boiled solution of ferrous chloride placed in the bulb, and allowed to pass into the flask by slightly raising the second tube. Afterwards 40 c.c. of concentrated boiled hydrochloric acid is added in a similar manner. As soon as the liquid boils, the current of carbonic anhydride is cut off, and only renewed towards the end of the operation, when the contents of the flask become thick. With this apparatus, it is necessary to employ reagents from which the air has been previously expelled by boiling.

H. G. C.

Estimation of Arsenic. By F. W. BOAM (*Chem. News*, **61**, 219).—The following method is recommended as rapid and accurate, and is applicable to all arsenical ores which are attacked by nitric acid:—

1 to 1·5 gram of dry pulverised ore is boiled to dryness with 20 to 25 c.c. of nitric acid, and when cool is boiled with 30 c.c. of a 30 per cent. solution of sodium hydroxide, filtered, and diluted to 250 c.c. 25 c.c. of this solution is acidified with 50 per cent. acetic acid containing 10 per cent. of sodium acetate, boiled, and titrated with $\frac{1}{4}$ normal uranium acetate, using potassium ferrocyanide as an indicator.

D. A. L.

Estimating Silica in Silicates by Fusion with Alkaline Carbonates. By J. P. GILBERT (*Chem. News*, **61**, 270—272; 281—282).—The author, investigating the fusion method of estimating silica, determined under varying conditions the insoluble silica obtained, the silica passing into solution, and the residue left after treating the former with hydrofluoric acid. In the first set of experiments, a blast furnace slag, containing 46 per cent. of calcium oxide, 10 per cent. of alumina, and less than 1 per cent. of magnesium oxide, was employed, and the silica was dehydrated either on the water-bath, or at 125°, or on an iron plate over a Bunsen, or at 280°. The results show that, practically, all the silica is rendered insoluble on the water-bath, the soluble never exceeding a few tenths of a milligram, and therefore there is no gain in this respect by the use of higher temperatures, the effect of which seemingly is to render some of the alumina insoluble, as indicated by the residue left after treatment with hydrofluoric acid, but there is no evidence of re-combination of silica with lime and alumina even at 280°.

Calcium chloride appears to aid the dehydration, but magnesium chloride does not. In a second series of experiments with a slag containing 35 per cent. of calcium oxide, 15 per cent. of magnesium oxide, and 15 per cent. of alumina, it was observed that the best results were obtained at 120°, the residue after hydrofluoric acid and the soluble silica were, especially at 280°, moderately large—a few milligrams; owing, the former to magnesium oxide, the latter to recombination of silica and magnesium oxide.

A sample of orthoclase, practically free from lime and magnesia, yielded a moderate amount (2 or 3 milligrams) of soluble silica, not increased by the higher temperatures, which the author regards as the result of the absence of the beneficial factor, calcium chloride. It therefore appears that some silica always fails to be rendered insoluble by the heating alone, and to test this, some silica from the lime slag was repeatedly treated by fusion with alkaline carbonates in the usual way, with the result that a diminished amount of insoluble silica was obtained each time.

With regard to the purity of the silica obtained, the author applied Lindo's plan of copious dilution, which, permitting as it does of abundant washing, yields a pure silica when the silica is associated with alkalis or alkaline earths, as in glass; but when much alumina is present it is not so easy to obtain such pure silica by this means.

The results, as a whole, confirm the statement that the ordinary fusion process for the estimation of silica does not always render all

the silica insoluble. Evaporation with sulphuric acid is, however, far more potent than the use of hydrochloric acid for the dehydration, and should be employed when admissible.

D. A. L.

Caustic Soda or Potash and Carbon in Analysis. By C. A. BURGHARDT (*Chem. News*, **61**, 260—262).—The author suggests a method for the decomposition of refractory silicates, several refractory oxides and compounds of oxides, and some other insoluble minerals. The finely pulverised mineral, mixed without about a tenth of its weight of finely divided charcoal, is added to about six times its weight of molten caustic soda or potash, and heated over a Bunsen flame until combustible gases cease to be evolved. The mass is extracted with water, and the insoluble residue again treated in like manner. With a sample of "black tin" (dressed tin ore of Cornwall) sodium silicate, aluminate, and stannate were obtained in solution, whilst the insoluble residue contained silica, bismuth oxide, cupric oxide, ferric oxide, calcium carbonate, and manganese dioxide. Wolframite yields sodium tungstate, manganate, silicate, and niobate, if present, in solution, and iron oxides and manganese dioxide insoluble. With chrome iron ore, three times its weight of ammonium nitrate was placed, along with the caustic soda, on the mineral and charcoal mixture in the crucible and heated. The aqueous extract of the fused mass was evaporated to dryness with ammonium nitrate, and, after separating the alumina and silica, the filtrate when acidified with hydrochloric acid yielded chromic chloride without further reduction. The insoluble portion was ferric oxide, magnesium carbonate, carbon, &c. Rutile and ilmenite yield sodium titanite; barium sulphate gives barium carbonate and sodium sulphate. Simple silicates, such as kaolin, talc, cyanite, &c., and double silicates, such as tourmaline, hornblende, garnet, &c., are also decomposed and rendered soluble.

D. A. L.

New Method for the Estimation of Free and Combined Carbon in Iron and Steel. By O. PETTERSSON and A. SMITT (*Ber.*, **23**, 1401—1402).—A weighed quantity of iron, which should consist of one piece hammered or rolled into a thin sheet, is plunged into molten hydrogen potassium sulphate; the iron becomes converted into ferric sulphate, and the combined carbon is oxidised to carbonic anhydride, which, together with the evolved sulphurous anhydride, is absorbed by a known quantity of a solution of sodium and barium hydroxides.

The barium sulphite is oxidised to sulphate by the addition of a little potassium permanganate solution, the carbonate is then decomposed with nitric acid, and the carbonic anhydride determined in an apparatus described in another paper. The fused mixture of potassium hydrogen sulphate and ferric chloride is dissolved in hydrochloric acid, the graphite collected on a platinum funnel, filtered through asbestos, and the whole dried and weighed. A mixture of air and nitrous fumes is now passed through the funnel, which is heated to redness; so soon as all the graphite is burned, the funnel is again weighed and is then ready for another determination. The accuracy of

this method is from 0·06—0·02 per cent. From 0·2—0·8 gram of iron should be taken for analysis, the quantity depending of course on the amount of carbon contained in the sample. J. B. T.

Electrolysis of Metallic Phosphates. By E. F. SMITH (*Amer. Chem. J.*, 12, 329—336; compare Moore, Abstr., 1886, 921; Brand, this vol., p. 294).—This paper relates to the deposition of metals by the electrolysis of solutions of their phosphates in phosphoric acid, whereon is based a convenient method of separating them.

Copper from Iron.—A solution, containing 0·0996 gram of copper and 0·1700 gram of iron, was treated with 30 c.c. of disodium phosphate solution (sp. gr. 1·0358) and 4½ c.c. of phosphoric acid (sp. gr. 1·347), and made up to 125 c.c. A current generating 0·6 c.c. of oxyhydrogen gas per minute gave a deposit of copper weighing 0·0996 gram.

Copper from Aluminium.—Weight of copper, 0·0996 gram; of aluminium 0·1000 gram. Disodium phosphate, 20 c.c.; phosphoric acid, 3 c.c.; total dilution, 100 c.c. Current, 3 c.c. of oxyhydrogen gas per minute. Copper deposited, 0·0995 gram.

Copper from Chromium.—Copper, 0·0996 gram; chromium slightly more than 0·0996 gram. Disodium phosphate, 20 c.c.; phosphoric acid, 3 c.c. Dilution and current as in previous case. Weight of copper deposited, 0·0994 gram.

Copper from Zinc.—Zinc, 0·1500 gram; copper, disodium phosphate, and phosphoric acid as in previous experiment; dilution 100 c.c.; current, 0·15 c.c. oxyhydrogen gas per minute. Weight of copper deposited, 0·0993 gram.

Copper from Cobalt.—Cobalt, 0·0968 gram; copper, 0·0996. Conditions similar to those of preceding experiment, except the current 0·22 c.c. of oxyhydrogen gas per minute. Copper deposited, 0·0995 gram.

Copper from Nickel.—Copper, 0·0996 gram; nickel, 0·1105 gram. Conditions as in preceding experiment. Copper deposited, 0·0996 gram.

Copper from Cadmium.—The separation may be effected by using a fairly large excess of phosphoric acid and a current generating not more than 0·10 to 0·20 c.c. of oxyhydrogen gas per minute, when the copper is deposited.

The preceding experiments show that copper may be readily separated from other metals, under the conditions given, by using feeble currents. In all cases, before interrupting the current, the acid liquid was syphoned off and replaced by water, the deposits were washed with cold and hot water, but no alcohol or ether was used. The poles of the electrolysing battery were about ¾ inch apart.

Cadmium from Zinc, Nickel, Iron, Chromium, and Aluminium.—Cadmium may be separated from these metals, in a properly diluted solution containing free phosphoric acid, by currents giving 0·35 c.c. of oxyhydrogen gas per minute. The deposit is not so satisfactory as in the case of copper, but accurate results are obtained if concentration of the solution is avoided, and the poles of the electrolysing cell are about 1¼ inches apart. It is also desirable to slightly increase the current before disconnecting.

Silver cannot be satisfactorily deposited in solutions containing free phosphoric acid, but from an ammoniacal solution of the phosphate its liberation is rapid and satisfactory.

Manganese is deposited as dioxide from solutions containing nitric or sulphuric acids; but, in presence of an excess of phosphoric acid, this behaviour is not observed, a weak current separating only copper from a solution containing the two metals. G. T. M.

Electrolytic Separations. By E. F. SMITH and L. K. FRANKEL (*Amer. Chem. J.*, **12**, 428—435; compare also this vol., pp. 664 and 831).—The metals were held in solution in excess of potassium cyanide, and deposited by means of a current from Daniell cells running for 16 hours. The deposited metal was washed with boiling water, or in the case of bismuth with cold water and absolute alcohol, and dried on a warm iron plate. In the following, the metal which is deposited on electrolysis is mentioned first:—

Mercury from Palladium.—Results good; a large excess of potassium cyanide should be present.

Silver and cadmium could not be separated in this way from palladium; some of the latter metal was always deposited.

Mercury from Arsenic.—Results satisfactory; the arsenic may be present either as arsenite or as arsenate.

Cadmium from Arsenic.—Results good; the arsenic must be in the form of an arsenate.

Silver from Arsenic.—Results satisfactory; the arsenic must be present as arsenate, not as arsenite.

Copper from Arsenic.—Results good, but a stronger current (giving 1·5 to 10 c.c. of mixed gases per minute in a water-voltameter) is required, and a large excess of potassium cyanide is not advisable. The separation was also attempted in solutions containing excess of ammonia, and with fairly good results, but considerable skill and attention are necessary.

Mercury from Tungsten.—Results good, but the current should not exceed 0·8 c.c. per minute, otherwise the deposit of mercury is contaminated with oxide of tungsten.

Silver from Tungsten.—Results good; the current must not be too strong.

Cadmium from Tungsten.—Results good, but too high if the current exceeds 0·6 c.c. per minute, when the deposit is spongy.

Mercury from Molybdenum.—Results good.

Silver from Molybdenum.—Results good.

Cadmium from Molybdenum.—Results good.

Bismuth from Copper.—The bismuth was taken as the citrate. dissolved in excess of alkali, and copper sulphate and excess of potassium cyanide added; satisfactory results were obtained.

C. F. B.

Quantitative Separation of Titanium and Tin. By H. HAAS (*Chem. Centr.*, 1890, i, 732—733; from *Inaug. Diss. Erlangen*).—The method described by the author is recommended as being applicable for the separation and determination of minute quantities of titanium, and is as follows:—5 to 10 grams of the finely-divided mineral is mixed

with a little water in a platinum crucible, dilute (1 : 10) sulphuric acid added until the mass is of a thin consistence, it is then warmed on the water-bath until, with additions of hydrofluoric and sulphuric acids, the mineral is dissolved. 10 to 20 c.c. of sulphuric acid is then added, the solution concentrated, and finally the last traces of hydrogen fluoride expelled by careful heating over a bare flame. Water is now added, the solution digested on the water-bath, and then transferred to a sufficiently capacious porcelain dish. It is neutralised with sodium hydroxide solution, 2 c.c. of concentrated sulphuric acid added, the volume made up to 400 c.c., and boiled for six hours, water being added to replace that which evaporates. The precipitate is collected, washed with hot water, and after diluting so that the sulphuric acid is not more than 0·5 per cent., the filtrate is boiled again to test whether the precipitation is complete.

The precipitate is ignited in a porcelain crucible, then washed on to a filter and washed with water, dried, and ignited again in a porcelain crucible, and finally reduced in a current of hydrogen. The metals are boiled with 20 per cent. hydrochloric acid for half-an-hour, filtered, and the insoluble portion again reduced in hydrogen and boiled with hydrochloric acid. The filtrates, containing all the tin, are neutralised with sodium carbonate, slightly acidified with hydrochloric acid, precipitated with hydrogen sulphide, filtered, washed with dilute ammonium acetate solution, and the filtrate again treated with hydrogen sulphide. The stannous sulphide is reduced in hydrogen, converted into metastannic acid, and finally weighed as stannic oxide.

That portion of the metals which remains insoluble in hydrochloric acid, the titanium dioxide, is ignited in a platinum crucible, fused with 6 to 10 times its weight of potassium carbonate, digested in water, diluted to 200 c.c., and acidified with sulphuric acid until the solution is clear or slightly opalescent. Sodium carbonate is now added until the precipitate commences to be permanent, 2 c.c. of concentrated sulphuric acid added, the liquid diluted to 400 c.c., and boiled for six hours in a capacious porcelain dish, the precipitate filtered off, washed with hot water, the filtrate boiled again to ensure that the precipitation is complete, and the precipitate heated in hydrogen. Traces of iron are removed by boiling for half-an-hour with 20—30 c.c. of hydrochloric acid. The insoluble titanium dioxide is washed and weighed as such. J. W. L.

New Method of Titrating Alcohol with Chromic Acid. By R. BOURCART (*Chem. Centr.*, 1890, i, 547; from *Bull. Soc. Ind. Mulhouse*, **59**, 558—562).—The author adds potassium dichromate and sulphuric acid to the alcohol in tubes, which are closed by stoppers tightly fastened down, and heats the same for 2 to 3 hours on the water-bath. After the oxidation is completed, potassium iodide is added and the liberated iodine titrated with sodium thiosulphate. The strength of the potassium dichromate solution used is 0·5 per cent.; the sulphuric acid is 25 per cent., and the alcohol should be about 0·5 per cent.

Aldehyde may also be determined in the same way. The method gives results which agree within about 1·5 per cent. J. W. L.

Raisin Wines and their Richness in Nitrogen. By P. Cazeneuve and L. Ducher (*Bull. Soc. Chim.* [3], **3**, 514—518).—The authors review the methods suggested for distinguishing between raisin and grape wines, and conclude that no satisfactory process exists. They have determined the total nitrogen in both classes of wines, and find that in dry white wines the total nitrogen is almost identical, but that in sweet white wines a difference of about 0·5 gram per litre of total nitrogen exists. T. G. N.

Estimation of Sugars with Copper Potassium Carbonate Solution. By H. Ost (*Ber.*, **23**, 1035—1039).—Copper carbonate dissolves freely in a cold concentrated solution of potassium carbonate, yielding a deep-blue solution of a readily soluble double salt, which crystallises in slender, blue needles; if the solution is heated, a basic copper carbonate or the black oxide is deposited, but in presence of a sufficient quantity of potassium hydrogen carbonate, the solution is quite stable, even at its boiling point, and can be advantageously employed for the volumetric or gravimetric estimation of sugars.

The standard solution is prepared by dissolving potassium carbonate (250 grams) and potassium hydrogen carbonate (100 grams) in water, gradually adding a solution of crystalline copper sulphate (23·5 grams), and making up to 1 litre. 50 c.c. of this solution is exactly decolorised by 9 to 10 minutes' boiling with 25 c.c. of a 0·4 per cent. solution (= 100 milligrams) of pure inverted sugar. The end of the reaction can be easily and accurately observed by the disappearance of the blue colour, and the liquid is then quite clear, not yellow, as is the case with Fehling's solution. In presence of cane-sugar, slightly smaller quantities of the inverted sugar solution are required. In the case of cane-sugar solutions very poor in inverted sugar, a copper solution containing one-fifth of the above quantity of copper sulphate is employed; this dilute solution has hardly any action on pure cane-sugar. The weight of the cuprous oxide precipitated by various quantities of inverted sugar, in presence and in absence of cane-sugar, is given in tables. F. S. K.

Detection of Benzoic Acid in Foods. By E. Mohler (*Bull. Soc. Chim.* [3], **3**, 414—416).—The author employs the reaction of hydrogen sulphide on an ammoniacal solution of dinitrobenzoic acid (1 : 3 : 5), which determines the formation of reddish-brown ammonium diamidobenzoate [1 : 3 : 5]. In the case of beer, 100 c.c. is rendered alkaline by sodium hydroxide, and evaporated to a paste, which, after acidifying with hydrochloric acid, is mixed with sand and extracted with ether (20 c.c.). After evaporation of the ether, the residual extractive is sprinkled with sulphuric acid (2 c.c.), heated at 210°, and a few decigrams of sodium nitrate are added, the clear liquid formed is poured into ammonia-water, and a drop of ammonium hydrosulphide added, when a reddish-brown coloration will indicate benzoic acid if present. A few tenths of a milligram of benzoic acid may be thus detected. T. G. N.

Occurrence and Detection of Indigo-red in Urine. By O. ROSENBACH (*Zeit. anal. Chem.*, **29**, 240; from *Berlin klin. Wochensch.*, 1889, 13. 17. 22, 23).—Certain pathological urines, when oxidised by nitric acid, yield a deep burgundy-red to blue-red colour, which, by further action of nitric acid, passes into yellow. To the fresh urine, decolorised by lead acetate, filtered, and heated to boiling, nitric acid is added drop by drop until the purple colour is produced; the heating is then stopped, and ammonia added to alkaline reaction, whereon the red colouring matter is precipitated in an impure state. It is collected, washed with ammonia, dilute hydrochloric acid, and water, then dissolved in boiling alcohol. The solution deposits indigo-blue on cooling. The filtrate is purified from a brownish substance by alcoholic lead acetate, and most of the alcohol distilled off. The residue is mixed with much water, when a dark-brown powder separates, which, after crystallisation from ether or chloroform, shows the reactions of indirubin. A small specimen of the urine may be tested by adding nitric acid while boiling, then cooling, supersaturating with ammonia, and shaking with ether. A purple coloration of the ether shows the presence of indirubin. Urines which contain the chromogen of indigo-red give a more or less pronounced violet colour with Jaffé's indican test. M. J. S.

Analysis of Resins and Balsams. By M. BAMBERGER (*Monatsh.*, 11, 84—86).—The author has examined a number of resins and balsams in order to determine their methyl-number, and has made use of the method and apparatus described by Benedikt and Grüssner (this vol., p. 299). The results are given in tabular form; and it appears that a large proportion of the substances investigated contain no methoxyl. Of those which do, the most important are given with their methyl-numbers in the following list:—Gum ammoniacum, 11; asafœtida, 18; gum benzoin, 13·3—30; dragons' blood, 33·8; guaiacum resin, 84; myrrh, 13·2; olibanum, 5·3; balsam of Peru, 14·4; tolu balsam, 46·8; acaroïd resin, 26·4—32·7. G. T. M.

A Cyanogen Reaction of Proteïds. By J. GNEZDA (*Proc. Roy. Soc.*, **47**, 202—210).—The author modifies the "biuret reaction" (rose-red colour produced by biuret, peptones, and albumoses, on treatment with a solution of copper sulphate and a caustic alkali) in so far as he employs a solution of ammonia instead of the usual solution of caustic alkali, which may, however, afterwards be added. He finds that copper sulphate and ammonia added to albumin give a blue solution which becomes violet on addition of potash; peptones or albumoses treated with the first reagents give a violet solution which is turned red by potash. An ammoniacal solution of a nickel salt gives somewhat similar colour reactions. Various organic substances ultimately produced from proteïds were tested in the same way, and from the results of his experiments, the author concludes that the colour reaction with copper sulphate and an alkali is a cyanogen reaction, the difference in the colours obtained being attributable to different modes of combination of the cyanogen-group. J. W.

General and Physical Chemistry.

Concentration of the Sun's Rays for Chemical Reactions. By J. W. Brühl (*Ber.*, **23**, 1462).—The author has found a concave mirror very useful in starting and carrying out chemical reactions by the aid of sunlight. F. S. K.

Refractive Powers of Salts in Solution. By E. Doumer (*Compt. rend.*, **110**, 957—958).—The refractive powers of salts in solution are not constant, but in some cases increase with the concentration, in others decrease, the variations being especially marked in the case of dilute solutions. In comparing the refractive powers of different salts it is therefore essential that the conditions should be strictly comparable. The author finds that his laws of the molecular refractive powers (this vol., p. 433) hold good only when the state of dilution is such that the density of the salt in the solution, with respect to hydrogen, is equal to the molecular weight of the salt. By density of the salt is meant the weight of salt contained in a unit volume of the solution.

The different results obtained by Walter are due to the fact that this condition of concentration of the solution was not fulfilled, and also that Walter's refractive powers are given by the expression $\frac{n - n_0}{p}$, n being the index of refraction of the solution n_0, that of water, and p the weight of the anhydrous salt contained in 100 grams of the solution, whilst the author's refractive powers are calculated from the expression $\frac{n^2 - n_0^2}{d}$, where n and n_0 have the same significance as before, but d is the weight of the salt contained in a unit volume of the solution. For the same salt, d and p may be regarded as proportional, but this does not by any means hold between different salts. C. H. B.

Determination of the Molecular Refraction of Solid Chemical Compounds in their Solutions. By F. Schütt (*Zeit. physikal. Chem.*, **5**, 349—373).—The present paper deals with the examination of solutions of sodium chloride in water. The refractive indices for the potassium (red), sodium, lithium, thallium, and hydrogen, α, β, and γ lines, and the densities of solutions varying from 0·1 to 25 per cent. in concentration were determined with the greatest possible accuracy. From these the specific refraction was calculated by means of each of the three formulæ $(n - 1)d$ (Dale and Gladstone), $(n^2 - 1)/(n^2 + 2)d$ (Lorentz and Lorenz), and $(n^2 - 1)/(n^2 + x)d$ (Ketteler). The object was to ascertain with what accuracy the specific refraction of a concentrated salt solution might be determined from that of mixtures of the same with water, to determine the specific refraction of sodium chloride from that of

its solution, and to compare the value thus obtained with that observed with the solid salt itself; and to decide with what degree of accuracy the refractive index of any given salt solution may be calculated from the percentage composition and density, if the refractive indices of water and of a more concentrated solution are already known.

In the above calculations it is assumed that if p be the percentage of salt in the solution, R′ the specific refraction of the solution, R that of sodium chloride, and R″ that of water,

$$100R' = pR + (100 - p)R''.$$

It is then found that of the formulæ used to express the specific refractions of sodium chloride and its solutions, that of Ketteler gives the best results. Using this formula, the specific refraction of a concentrated salt solution may be calculated from that of any other solution containing more than 1 per cent. salt to within $\frac{1}{4823}$. The specific refraction of sodium chloride calculated from that of any of its solutions containing more than 1 per cent. salt will be found to vary only $\frac{1}{848}$ in amount. The value thus obtained can therefore be used for the calculation of the molecular refraction; it is not, however, identical with that obtained for sodium chloride by direct determination. With the above value, the refractive indices of salt solutions of any concentration can also be calculated from those of a more concentrated solution and of water, the agreement between the numbers thus calculated and those observed being to within five units of the fifth decimal place.

H. C.

Dispersive Power of Carbon Compounds. Alcohols of the Fatty Series. By P. Barbier and L. Roux (*Compt. rend.*, **110**, 1071—1074, compare Abstr., 1889, 805).—The following results were obtained:—

	$t°$.	A.	B.
Methyl alcohol	10·0	1·3244	0·318
Ethyl alcohol	14·0	1·3522	0·358
Propyl alcohol	15·0	1·3733	0·381
Butyl alcohol	14·1	1·3892	0·398
Amyl alcohol*	—	—	0·415
Hexyl alcohol*	—	—	0·422
Heptyl alcohol	16·4	1·4105	0·430
Octyl alcohol	16·3	1·4179	0·437
Isopropyl alcohol	15·4	1·3661	0·380
Secondary butyl alcohol	15·4	1·3852	0·396
Diethyl carbinol	14·3	1·3976	0·407
β-hexyl alcohol	15·4	1·4053	0·4215
Secondary heptyl alcohol*	—	—	0·428
Secondary octyl alcohol	16·6	1·4158	0·4355
Isobutyl alcohol	21·8	1·3827	0·394
Isoamyl alcohol	22·1	1·3940	0·406

* These values of B were obtained by interpolation.

	$t°$.	A.	B.
Allyl alcohol	13·4	1·4061	0·5385
Diallyl carbinol	16·6	1·4281	0·614

In the alcohols of the ethyl series, the dispersive powers are continuous functions of the molecular weights, and increase with the molecular weight, a result the reverse of that obtained with compounds of the benzene series. Primary and secondary alcohols have practically the same dispersive powers, but in the case of the isoprimary alcohols the values are slightly lower than for the corresponding normal primary compounds. The elimination of hydrogen results in a considerable increase in the dispersive power.

C. H. B.

Seat of the Variation of Electromotive Force with Temperature. By A. GOCKEL (*Ann. Phys Chem.* [2], **40**, 450—463).—The author takes four cells and places them at the corners of a rectangle, and then joins them up as required along the sides of the rectangle by means of siphons. The cells at one pair of adjacent corners contain, *e.g.*, a solution of zinc sulphate with zinc electrodes, the other pair containing copper sulphate solution and copper electrodes. This arrangement thus gives two Daniell cells, one of which can be warmed in a water-bath whilst the other remains cold; the necessary connections are made with the siphons. By suitable combination, the temperature coefficients of the different contacts may be determined, and from these the author calculates by summation the temperature coefficient of the whole galvanic element. The agreement between direct experiment and calculation is fairly satisfactory. J. W.

New Method and Department of Chemical Research. By G. GORE (*Phil. Mag.* [5], **29**, 401—427).—The author in this paper gives the results of his investigation on the change of electromotive force of a zinc-platinum element brought about by changing the concentration of the solutions of different substances in which the metals are immersed. The method employed was that of the "voltaic balance" (compare Abstr., 1889, 665), which is much more delicate than the thermopile method he formerly used. Increased concentration is usually accompanied by increased electromotive force, and chemically analogous substances give curves which show a general similarity to each other, but which are still perfectly characteristic of the different compounds. The effect of change of temperatnre at one and at both metals was also studied. The experimental results are given in the form of numerous curves, and a theoretical discussion follows. J. W.

Fall of Potential at the Cathode in Geissler's Tubes. By E. WARBURG (*Ann. Phys. Chem.* [2], **40**, 1—17).—This paper is a continuation of a former communication on the same subject (*Ann. Phys. Chem.* [2], **31**, 545).

The author had observed that whilst in a Geissler's tube filled with slightly moist nitrogen the difference of potential between the cathode and a point in the extreme visible limit of the negative glow remained

constant, yet when the nitrogen was quite dry, a considerable increase of fall took place as the current passed. This he now attributes to the presence of minute quantities of oxygen in the nitrogen, and shows in the present communication how these traces may be removed. Sodium had previously been used for this purpose, but a difficulty was experienced in obtaining this metal in a state of sufficient purity. The author liberates his sodium within the closed tube in the "nascent" state by electrolysis through the glass, a portion of the tube being immersed in half per cent. sodium amalgam connected with the negative pole of a battery and heated to 300°, the cathode of the tube being connected with the positive pole. When the last trace of oxygen has been removed a deep-yellow light appears in the part of the tube in which the sodium is liberated. Nitrogen at 2·3 mm. pressure was freed from oxygen in 20 minutes, with a current from three Bunsen cells connected with an induction coil capable of giving a 25 mm. spark in air, and making 390 contacts a minute. The excess of sodium was afterwards distilled into a remote portion of the tube. From his experiments the author gets the following mean numbers for the fall at the cathode in volts :—Platinum cathode: in nitrogen, 232; in hydrogen, 300. Magnesium cathode: in nitrogen, 207; in hydrogen, 168.

Variations of a few per cent. still remain, but the author is of opinion that in perfectly pure gases the fall is independent of the current strength and of the pressure, being determined only by the chemical nature of the gas and of the cathode, and by the physical condition of the latter. J. W.

Surface-tension of Polarised Mercury. By F. PASCHEN (*Ann. Phys. Chem.* [2], **40**, 36—52).—In continuation of a previous paper (this vol., p. 552), the author now investigates the effect of concentration of the electrolytic solution, and seeks to test Pellat's relation between the maximum of surface-tension and the point where electrolysis begins. For sulphuric and nitric acids, he finds that the maximum increases with increasing concentration, whilst the E.M.F. for incipient electrolysis diminishes. It thus happens that for a definite mean concentration the two values become equal, so that it is only for this concentration that Pellat's relation holds good. The fall beyond the maximum depends on the relative values of the E.M.F. for maximum surface-tension and for electrolysis. There is little or no fall for strong solutions of the above acids, when the E.M.F. for electrolysis is far below the maximum.

Other electrolytes investigated were solutions of nitric acid, ferrous sulphate, potassium hydroxide, potassium iodide, and mercuric cyanide. Nitric acid and ferrous sulphate behave very similarly to hydrochloric acid. The point for electrolysis is affected by the nature of the solvent (water, ethyl alcohol, amyl alcohol). A strong solution of potassium cyanide behaves abnormally, giving a deflection of the meniscus in a direction opposite to that when other electrolytes are employed. Experiments with electrometers containing Wood's metal instead of mercury led to identical results. J. W.

Passage of Electricity through Hot Gases. By J. J. Thomson (*Phil. Mag.* [5], **29**, 358—366, and 441—449).—The gases to be examined were contained in a platinum tube, into which the insulated terminals dipped. The tube was wrapped round with asbestos tape, placed in an outer iron tube, and the whole arrangement then put into a muffle furnace, heated by a gas-air blast. The electrodes were placed in circuit with a battery and a galvanometer of 4000 ohms resistance. When the gas had attained the temperature required, a reading of the galvanometer was made, the current reversed, and the opposite deflection observed.

Great differences were found in the behaviour of gases at a yellow heat. Air, nitrogen, sulphur, mercury, ammonia, steam, hydrogen sulphide, carbonic anhydride, nitric and sulphuric acids—all gave extremely small deflections; whereas bromine, iodine, hydrogen iodide, hydrogen chloride, and the vapour of several haloid salts, conducted well. To volatilise more refractory substances, such as silver and tin, the oxyhydrogen blowpipe was employed, the substances being contained in a hole made in a ganister brick. Mercury, thallium, and tin did not seem to conduct; but the vapours of the other metals, such as lead, aluminium, and magnesium, conducted much better than air, sodium and potassium being specially good conductors.

Whenever a gas became a good conductor on being heated, the author was able to detect dissociation by purely chemical means. All substances, however, which dissociate on heating do not necessarily conduct: ammonia and steam, for example. Conduction is only observed when the products of dissociation are atoms or unsaturated groups. The very slight conductivity in the case of air, &c., is probably due to convection of particles from the negative to the positive pole. Ohm's law seems to be approximately obeyed in the case of gases that conduct well. Cold metals are not capable of taking up electricity from hot gases, for no current is observed until both electrodes are red-hot. The nature of the electrodes seems to have no effect on the class of good conductors, neither does alteration of their relative size. No polarisation could be detected. Unsaturated gases, like NO and O_3, behaved exactly like air. J. W.

Electrical Conductivity of Fused and Solid Salts. By L. Graetz (*Ann. Phys. Chem.* [2], **40**, 18—35).—The author placed a quantity of the salt to be investigated in a small porcelain crucible, the lid of which contained four openings for the reception of the wires leading to the electrodes, and those of the thermo-element used to measure the temperature. The crucible was placed in a large sand-bath, and precautions taken that the conducting wires should be kept hot, so as to prevent solidification of the fused salt on the electrodes and on the junction. The bath was heated to considerably above the temperature of fusion of the salt, and then allowed slowly to cool, simultaneous determination of the temperature and the conductivity being made from time to time. The melting point was determined by a separate experiment. Tables are given for the conductivity of the following substances: the chlorides, bromides, and iodides of cadmium and zinc, lead chloride, lead iodide, potassium nitrate,

cuprous chloride, stannous chloride, and antimonious chloride. The results obtained serve to show that there is in no case a sudden change of conductivity at the melting point, as Foussereau (*Compt. rend.*, **98**, 1325) asserted. In conclusion, the author discusses at some length the theoretical aspect of the question, particularly in connection with dissociation. J. W.

Conductivity of the substituted Succinic and Glutaric Acids. By C. A. Bischoff and P. Walden (*Ber.*, 23, 1950—1958).—The authors have continued their investigation of the conductivity of the substituted succinic acids (this vol., p. 745; see also Bethmann, *Zeit. phys. Chem.*, 5, 385), with the results given in the following table, in which K represents 100 times the dissociation constant:—

Substance.	Melting point.	K.
Trimethylsuccinic acid	105°	0·0054
h-Propyldimethylsuccinic acid	51—53	0·0054
h-Ethyldimethylsuccinic acid	62	0·0057
H-Ethyldimethylsuccinic acid	105	0·0059
H-Propyldimethylsuccinic acid	101—102	0·0059
Benzyldimethylsuccinic acid	128—130	0·0059
Succinic acid	180	0·00665 (Ostwald)
Asymmetrical dimethylsuccinic acid	140	0·0080
Ethylsuccinic acid	98	0·0083
Methylsuccinic acid	112	0·0086
Benzylsuccinic acid	161	0·00905
Antidimethylsuccinic acid	120	0·0122
Paradimethylsuccinic acid	194	0·0190
Mesoethylmethylsuccinic acid	88	0·0201
Paraethylmethylsuccinic acid	168·5	0·0206
Parabenzylmethylsuccinic acid	159—160	0·0219
Paradiethylsuccinic acid	192	0·0245
Mesobenzylmethylsuccinic acid	137—138	0·0247
Parabenzylethylsuccinic acid	154	0·0262
Tetramethylsuccinic acid	190—192	0·0314
Antidiethylsuccinic acid	128	0·0343
Mesobenzylethylsuccinic acid	123	0·0414

It will be seen that the trisubstituted succinic acids have the least conductivity, and also differ least among themselves.

Similar measurements have also been made with several of the substituted glutaric acids. As has been previously pointed out, the compounds described above as trisubstituted succinic acids may possibly be in reality disubstituted glutaric acids. They are therefore also included in the following table:—

Substance.	Melting point.	K.
Trimethylglutaric acid	97°	0·00352
Glutaric acid	97·5	0·00475
α-Symmetrical dimethylglutaric acid	126—127	0·0053
β- " " "	102—103	0·0055
Dimethylglutaric acid	99—101	0·0054
Trimethylsuccinic acid	105	0·0054
α-Methylglutaric acid	76	0·0054
h-Propyldimethylsuccinic acid = mesopropylmethylglutaric acid	51—53	0·0054
α-Symmetrical diethylglutaric acid	113—114	0·0055
h-Ethyldimethylsuccinic acid = mesoethylmethylglutaric acid	62	0·0057
H-*Ethyldimethylsuccinic acid* = paraethylmethylglutaric acid	105	0·0059
H-*Propyldimethylsuccinic acid* = parapropylmethylglutaric acid	101—102	0·0059
Benzyldimethylsuccinic acid = benzylmethylglutaric acid	128—130	0·0059

The differences in this case are too small to allow of the deduction of any conclusions concerning the constitution of the different acids.

H. G. C.

Conductivities of the Ammonium and Aniline Salts of the Hydroxybenzoic Acids. By D. BERTHELOT (*Compt. rend.*, **110**, 1066—1069).—The conductivity of mixtures of phenol and ammonia is considerably greater than the mean calculated conductivity, the difference being at a maximum with equal equivalents of phenol and the alkali. This also holds good for mixtures of benzoic acid with ammonia. The conductivity of ammonium benzoate when the base and acid are present in equivalent proportions, or where the benzoic acid is in excess, is greater than that of sodium benzoate.

In the case of orthohydroxybenzoic acid and ammonia in different proportions, the conductivities are always considerably less than the calculated values, but with the meta- and para-hydroxybenzoic acids the results are of the same kind and same order of magnitude as with benzoic acid. Notwithstanding the great differences between the conductivities of the three acids, the conductivities of mixtures of the acids with an equivalent quantity of ammonium are practically identical. A similar result was obtained previously with the sodium salts, the conductivity of which is somewhat lower. With orthohydroxybenzoic acid the maximum difference between the observed and calculated conductivities is given by a mixture of equal equivalents of the acid and the base; in the case of the meta- and para-acids the difference increases with the addition of a second equivalent of ammonia. A strictly analogous result was obtained with the sodium salts.

The observed conductivities of mixtures of aniline and benzoic acid are practically identical with the calculated values, and it follows that the aniline benzoate is completely dissociated in the solution. With

orthohydroxybenzoic acid and aniline, the observed values are decidedly less than the calculated, and there is evidently considerable combination; with the meta- and para-acids, the results are almost the same as with benzoic acid, and there is very little combination. The observed values are slightly less than the calculated for the meta-acid, and slightly greater for the para-acid. C. H. B.

Electrolysis of Aluminium Fluoride in Igneous Fusion. By A. MINET (*Compt. rend.*, **110**, 1190—1193).—Aluminium sodium chloride, even when mixed with excess of sodium chloride, is too volatile to be used economically as an electrolyte. A mixture of 40 parts of aluminium sodium fluoride with 60 parts of sodium chloride is practically non-volatile below 1100°, and is sufficiently fluid at 800°. Electrolysis with carbon electrodes follows the ordinary laws of electrolyis of solutions. The composition of the electrolyte can be kept constant by repeatedly adding aluminium fluoride, but as this involves the loss of a quantity of fluorine equivalent to the aluminium deposited, a mixture of fluoride and oxide corresponding to the oxyfluoride, $Al_2O_3 \cdot Al_2F_6$, is used. The electrolytic cell is a cubical steel vessel, and in order to prevent corrosion, 5 per cent. of the current of the cathode is diverted by means of a resistance, and thus the internal surface of the cell is kept coated with a very thin layer of aluminium.

In one experiment with four cells, the temperature of the fused salt being 1100°, and the duration of the experiment 21 hours, the constants for a single cell were: difference of potential, 5·75 volts; intensity, 1500 amperes; E.M.F. of decomposition, 2 volts; resistance of electrolyte, 0·0025 ohm, and weight of metal deposited 5250 grams. C. H. B.

Determination of the Heat of Vaporisation by Means of the Steam Calorimeter. By K. WIRTZ (*Ann. Phys. Chem.* [2], **40**, 438—449).—With the steam calorimeter of Bunsen and Joly, the author finds it is easy to determine with considerable accuracy the heat of vaporisation of liquids boiling below 100°. The vessel in which the liquid is contained is a test tube 23 mm. wide and 75 mm. long, surrounded by a loosely-fitting glass jacket 55 mm. long. This test tube is placed in the platinum basket, and the increase of weight noted on immersing it in steam. A second experiment is then made with the same apparatus, plus a weighed quantity of liquid. From the two weighings the quantity of steam condensed owing to the vaporisation of the liquid can easily be obtained. For precautions against spurting and overheating, the original paper must be consulted. The results of the author's experiments agree very well with those of Regnault, Andrews, and others. J. W.

Heat of Formation of Uric Acid and Alkaline Urates. By C. MATIGNON (*Compt. rend.*, **110**, 1267—1270).—Heat of combustion of 1 gram of uric acid in the calorimetric bomb, 2,754 Cal.; molecular heat of combustion at constant volume, 462·7 Cal., at constant pressure, 461·4 Cal.; heat of formation, +148·1 Cal.

Potassium Urates.—Heat of dissolution of the bibasic urate in dilute potassium hydroxide, $-6{\cdot}0$ Cal., $C_5H_4N_4O_3$ sol + 2KOH sol. = $C_5H_2N_4O_3K_2$ solid $+2H_2O$ develops $+37{\cdot}5$ Cal. Heat of formation of the bibasic urate, $+256{\cdot}2$ Cal.

Heat of dissolution of the monobasic urate, $-8{\cdot}4$ Cal.; heat of neutralisation of solid uric acid by the first equivalent of solid potassium hydroxide, $+23{\cdot}9$ Cal.; heat of formation, $+207{\cdot}0$ Cal.

Heat of neutralisation of the solid monobasic urate by a second equivalent of solid potassium hydroxide, $+13{\cdot}9$ Cal.; heat of neutralisation of the dissolved salt by dissolved potash, $+4{\cdot}6$ Cal. It follows from the thermochemical results that the second acid function of uric acid is of a phenolic rather than an acidic character.

Sodium Urates.—Heat of dissolution of the hydrated bibasic urate, $C_5H_2N_4O_3Na_2,H_2O$, in dilute sodium hydroxide solution, $-1{\cdot}4$ Cal. Heat of neutralisation of uric acid by two equivalents of sodium hydroxide in solution, $+6{\cdot}2$ Cal., in the solid state, $+27{\cdot}2$ Cal. Heat of formation of the hydrated bibasic urate, $+310{\cdot}9$ Cal.; of the anhydrous salt, $+240{\cdot}5$ Cal.

Heat of dissolution of the monobasic urate dried at 100°

$$C_5H_3N_4O_3Na,\tfrac{1}{2}H_2O,\ -8{\cdot}8\ \text{Cal.};$$

heat of neutralisation of solid uric acid by one equivalent of solid sodium hydroxide, with formation of the hydrated salt, $+21{\cdot}7$ Cal.; heat of formation, $237{\cdot}6$ Cal.; heat of formation of the anhydrous salt, $198{\cdot}5$ Cal. It follows from these results that uric acid should decompose sodium and potassium phosphates with formation of the monobasic phosphates, and this is found to be the case. Heat of neutralisation of the dissolved monobasic urate with formation of the dissolved bibasic salt $-5{\cdot}7$ Cal.; heat of neutralisation in the solid state, $+10$ Cal.

Ammonium Urate.—Molecular heat of combustion of the monobasic salt, $+530$ Cal.; heat of formation, $+183$ Cal.; heat of combination of gaseous ammonia with solid uric acid, $+22{\cdot}7$ Cal. The bibasic salt could not be obtained.

Uric acid has only one truly acid function; the bibasic urates are analogous to the phenolates and the tribasic phosphates.

C. H. B.

Heat of Transformation of Isomeric Inosites. By BERTHELOT (*Compt. rend.*, **110**, 1244—1246).—The heat of solution of dextrogyrate inosite at 17·9° is $-2{\cdot}05$ Cal., and that of lævogyrate inosite $-2{\cdot}03$ Cal. The two numbers may therefore be taken as identical, and the mean is $-2{\cdot}04$ Cal. No thermal disturbance is observed when the two solutions are mixed.

Heat of dissolution of racemic inosite, $-3{\cdot}87$ Cal., or $-7{\cdot}74$ Cal. for the double molecule; it follows that the heat of combination of the two optically active inosites is $+3{\cdot}66$ Cal. Inactive nonracemic inosite from walnuts has a heat of dissolution $-3{\cdot}38$ Cal. These numbers are of the same order of magnitude as in the case of the tartaric acids.

C. H. B.

Specific Gravity, Specific Heat, and Heat of Dissolution of supersaturated Salt-solutions. By K. BINDEL (*Ann. Phys. Chem.*, [2], **40**, 370—398).—This research comprehends solutions of magnesium sulphate, potassium chlorate, lead nitrate, sodium acetate, ammonium and potassium alums. With regard to the specific gravity of concentrated and supersaturated solutions of the above substances, the author finds that the numbers obtained are in fair agreement with those calculated from Valson and Bender's "moduli." By adopting E. Wiedemann's mode of treating the properties of solutions, he comes to the conclusion that "the specific gravity of the salt in solution is the greater, the more concentrated the solutions are." In a similar way he finds that the specific heat of the salt in solution diminishes with increasing concentration. The experimental results are expressed in numerous tables and curves. J. W.

Determination of Vapour Density. By C. SCHALL (*Ber.*, **23**, 1701—1705).—In the apparatus described in the author's previous paper (this vol., p. 681), toluene, aniline, and phenanthrene may be employed as heating liquids. To employ sulphur, a double Bunsen burner must be employed, and a small beaker, 9 c.m. in height, the bottom of which has an area of about 12 sq. c.m. The heating flask B. (see fig. *loc. cit.*) must then have a capacity of 22—23 c.c. In this manner the vapour density of substances boiling up to 450° can be determined. Under diminished pressure, the vapour density of substances boiling as high as 500° can be determined with a heating bath of 360°.

To obtain accurate results, the following precautions should be used: commercial sodium carbonate may be employed, but should be ignited and allowed to remain over sulphuric acid before being used, and the acid may be saturated by previously throwing into it a few grains of the carbonate. The indiarubber connections should be smeared inside and out with vaseline, and covered with gypsum or asbestos. The manometer tube in the author's experiments had a diameter of 2·6 mm., but a width of 4 mm. is not too large.

If the bulb be of 100 c.c. capacity, the quantity of substance taken should be at least 0·04 gram; with a bulk of 22·23 c.m., at least 0·01 gram. The errors are not greater than in the ordinary simpler methods of vapour density determination.

To carry out the determination in an indifferent gas, mercury purified by V. and R. Meyer's method is employed, and pure carbonic anhydride passed into the apparatus by means of an entrance tube at *e.* (see Fig., *loc. cit.*), and the substance, enclosed in a glass tube, then introduced into the caoutchouc tube *e*. For determining the vapour density under diminished pressure, the caoutchouc tube *e*, must consist of thick-walled pump tubing, and the heating-flask should not be too thin walled. If the latter has a capacity of 100 c.c., and the pressure be 30 mm., the quantity of substance taken should be about 0·0030 gram, if the density of the substance is nearly the same as that of air; this must be increased, however, as the density of the vapour increases; thus for a compound having a vapour density of about 11 (corr. = 1) the quantity should be about 0·03 gram. For

the reduction of the pressure, an ordinary water pump may be employed.

The results obtained with sulphur do not show any grounds for assuming the existence of the molecule S_6, and are thus in agreement with Biltz's results (Abstr., 1888, 1028). On the other hand, the density in diphenylamine vapour agrees fairly well with the molecular formula S_8, previously deduced by Beckmann (this vol., p. 447) from the rise in the boiling point of its solutions.

H. G. C.

Laws of Molecular Volumes and of Boiling Points. By C. M. GULDBERG (*Zeit. physikal. Chem.*, **5**, 374—382).—The molecular volumes of liquids are ordinarily compared at their boiling points, that is, at temperatures corresponding with equal vapour-pressures. For obvious reasons this comparison should be made under strictly comparable conditions; and this would only be the case when pressure, volume, and temperature were expressed in terms of their critical values. That certain regularities in the molecular volumes at the boiling points have in spite of this been discovered, is explained on comparing the values of T (the absolute boiling point) with those of T_1, the absolute critical temperature, in those cases in which these two constants are known. The ratio T/T_1 is found to be not absolutely constant, but in all cases the value obtained approximates to 2/3. Hence it follows that qualities like the molecular volumes which only alter slowly with the temperature, are practically comparable at the boiling points.

Since the critical pressure of liquids is generally very much greater than that of the atmosphere, Gay-Lussac's and Boyle's laws may be looked on as applicable at the boiling point. If V is the volume of the saturated vapour, then $pV = BT/m$, or $mV = BT/p$. Here B/p would be a constant quantity which by a suitable choice of units might be made equal to unity, in which case the absolute boiling point would obviously be a measure for the molecular volume of a saturated vapour under a pressure of 1 atmosphere. H. C.

Improvements in the Apparatus for Crystallising at a Low Temperature and in absence of Moisture and Air. By J. W. BRÜHL (*Ber.*, **23**, 1460—1461).—The improvements relate to the apparatus previously described (Abstr., 1889, 464). Instead of making an air-tight joint between the glass receiver (B) and the shallow bell-jar cover by means of an indiarubber ring, the edges of both are ground and greased, those of the receiver being turned slightly inwards at the top so that the greased surface forms a slight angle with the vertical. Instead of a platinum cone a marble is placed in the funnel-shaped portion of the receiver (B); it is then possible to apply greater pressure to the crystalline mass remaining in the receiver. The vessel containing the freezing mixture is wrapped round with flannel and covered with a felt plate.

The author finds that a marble placed in a funnel instead of a perforated plate, without either paper or cloth, forms a very good filter even for substances in a moderately fine state of division.

F. S. K.

Constitution of Solutions. By F. RÜDORFF (*Ber.*, **23**, 1846—1851; compare Abstr., 1888, 342, 889, and 1889, 98).—The previous researches of the author on the diffusion of double salts, have led him to divide them into two classes; the members of the first behave like a mixture of two simple salts, whilst those of the second act as definite chemical compounds. The object of the present research was to determine whether two salts, which do not react, behave towards each other when in solution in a manner at all comparable with a mixture of two indifferent gases. It is assumed that if the salts exert any mutual action, their combined effect on the solvent will be less than the sum of the influence of each separately. The method adopted consisted in determining the freezing point of various solutions. The following salts were investigated; the value t/g represents the constant depression of the freezing point caused by g parts of substance dissolved in 100 parts of water; the numbers are in all cases the mean of several experiments :—

	t/g.
Ammonium chloride	0·655
„ sulphate	0·277
Potassium chloride	0·462
Sodium „	0·604

The observed freezing point of mixtures of any two of these salts agreed very closely with the calculated numbers, showing that no interaction takes place. On the other hand, the freezing point of solutions of substances which form double salts, such as mixtures of mercuric cyanide and potassium cyanide; cupric chloride and ammonium chloride; aluminium sulphate and ammonium sulphate, &c., was always lower than that of the separate solutions. J. B. T.

Solid Solutions and Molecular-Weight Determinations of Solid Substances. By J. H. VAN'T HOFF (*Zeit. physikal. Chem.*, **5**, 322—339).—The well-known laws of the reduction of the freezing points of solutions by dissolved substances have now been satisfactorily established for 18 different solvents. The investigation of this subject has, however, brought to light a number of exceptions to the general laws which as yet remain unexplained. Many of these the author assumes to be due to the fact that in certain cases the substance which separates out on freezing is not the pure solvent, but a solid solution of the dissolved substance in the solvent. The properties of solid solutions are, therefore, discussed in order to ascertain what the effect of this behaviour would be.

As instances of solid solutions, we have isomorphous mixtures and mixed crystals, amorphous solutions, as in the case of the glasses and certain minerals; and then such cases as the solution of hydrogen by palladium and other metals. In solid solutions, diffusion can apparently take place as in liquid solutions. Spring has shown that double decomposition takes place between solids under pressure, and this decomposition must be preceded by diffusion. Glass behaves as an electrolyte, in which case diffusion of ions takes place through the mass. It is also known that carbon has the power of diffusing

through iron and porcelain. We may therefore assume that in solid solutions we have osmotic pressure, as in liquid solutions; and, if this is of kinetic origin, the laws applying to the latter will also apply to the former case. Hence the gaseous laws should be applicable to dilute solid solutions; and if this be the caso the osmotic pressure will be proportional to the concentration. In the case of the absorption of hydrogen by palladium this seems to be so. Up to a certain point, hydrogen is absorbed under a constant pressure of 225 mm. until 600 parts by volume have been taken up, corresponding with the formation of Pd_2H; but above this point the hydrogen absorbed is proportional to the pressure, as is seen by the following numbers:—

Massive palladium.			Spongy palladium.		
v.	P.	$P/v - 600$.	v.	P.	$P/v - 600$.
809	1428	6·8	775	715	4·1
743	909	6·4	743	493	3·5
700	598	6·0	718	361	3·0
672	454	6·3	684	247	3·0
642	353	8·4	—	—	—

The analogy between liquid and solid solutions would, further, lead to the conclusion, that the vapour-pressure of a solid would be reduced on its taking any other substance into solution. This view is supported by the fact that many isomorphous mixtures are more stable, and do not so readily undergo efflorescence as either of their constituents. This reduction of the vapour-pressure of a solid by the introduction of foreign material is of importance in considering the effect which the separation of a solid solution in place of the pure solvent has on the lowering of the freezing point. For, since the freezing point of a solution is the point at which the vapour-pressure of the solution and of the separating solid is the same, the smaller the vapour-pressure of the solid the higher will be the melting or freezing point of the solution. Hence the separation of a solid solution from a solvent in place of the pure solvent would make the freezing point fall too high, or would cause too small a depression of the freezing point. This is, as a matter of fact, what so often comes under observation, particularly in those cases in which the formation of a solid solution by the union of solvent and dissolved substance might from the first be expected. This is the case with solutions of metacresol and parabromophenol in phenol, of aldoxime in acetoxime, and of thiophen and pyridine in benzene.

By the application of the Raoult methods to solid solutions, these, like liquid solutions, should be made available for molecular-weight determinations. Although nothing has as yet been done in this direction, it is of importance to note that, from the fact stated above, that there is proportionality between the amount of hydrogen absorbed by palladium and the pressure of the gas, we may conclude

that free hydrogen and that held in solution by palladium have the same molecular composition. It is highly probable that the further study of solid solutions would throw much light on the question of the molecular structure of solids. H. C.

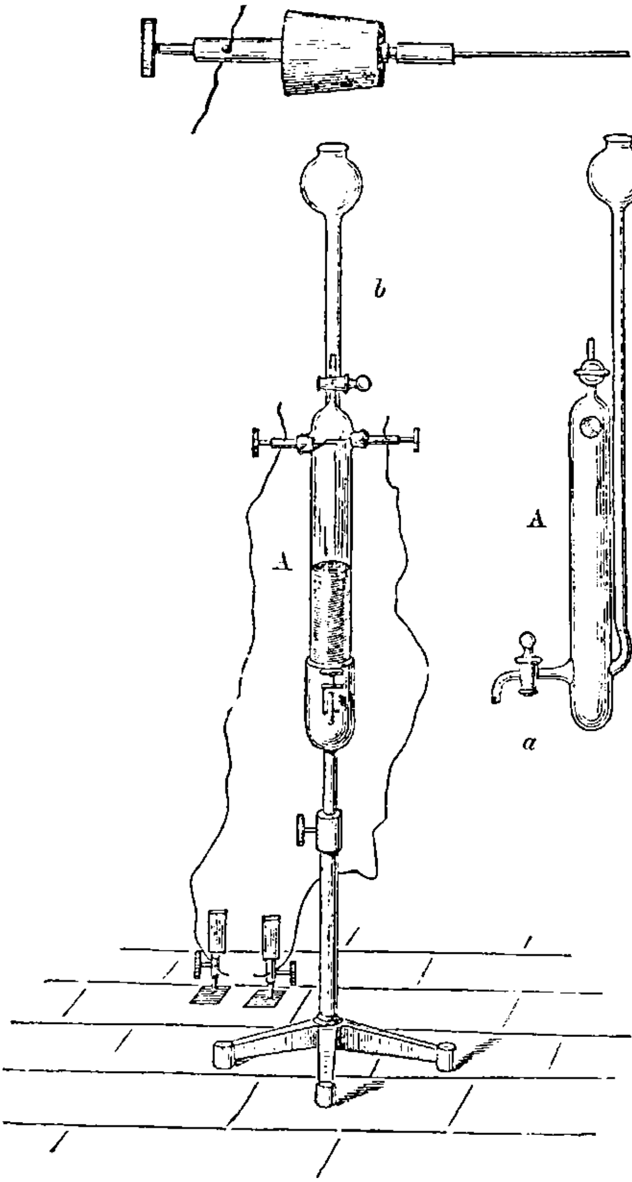
Possibility of Determining the Molecular Weights of Metals by two new Methods. By V. v. TÜRIN (*Zeit. physikal. Chem.*, **5**, 340—348).—The first method consists in measuring the E.M.F. of a simple galvanic cell, in which one electrode is formed of pure mercury, and the other of an amalgam of the metal, the molecular weight of which is being determined, the electrolyte being a mercury salt, either in solution in water or alcohol, or in the molten condition. The second method consists in measuring the E.M.F. of a simple galvanic cell, in which both electrodes are formed of amalgams of the metal, the molecular weight of which is being determined, of different concentrations, the electrolyte in this case being a salt of the same metal.

In the first instance, if we have two vessels, A and B, of which the first contains pure mercury and the second the amalgam, a cycle of changes may be performed by transferring osmotically a certain small quantity of mercury from A to B, and then connecting A with B electrolytically, and thus allowing the mercury to be returned to A. The work done in each of the above stages is of course the same, and is measured by the product of the E.M.F. into the amount of electricity, which is necessary to transfer unit weight of mercury from A to B, the latter being inversely proportional to the electro-chemical equivalent of mercury. The function may then be found which expresses the relation between the unknown molecular weight and the E.M.F. of the cell. The second method is in principle similar to the first, and differs from it only in being somewhat more complicated and difficult to treat. H. C.

Determination of Affinity Coefficients. By W. HECHT, M. CONRAD, and C. BRÜCKNER (*Zeit. physikal. Chem.*, **5**, 289—321; see these Abstracts, 1889, 931, and this vol., pp. 4, 327).—This paper deals with the influence of dilution on the rate of formation of ethereal salts. The action of sodium ethoxide on methyl iodide and its higher homologues is studied, the concentration of the solutions being varied from the normal, $v = 1$, to $\frac{1}{80}$ of the normal, $v = 80$. The combined influence of temperature and concentration on the affinity coefficients may be expressed by the following equation $k_v^t = k_1^t 10^{a'}(1 + \lambda \log v)$, in which $\lambda = 0{\cdot}4546$ for methyl, $0{\cdot}6058$ for ethyl, and $0{\cdot}7843$ for all the other alkyl iodides. The relation between the affinity coefficients does not vary greatly with rising dilution in the case of the higher alkyl iodides, ethyl iodide, however, shows a slight variation, and methyl iodide a very marked one, in the relation of their affinity coefficients at different dilution. For infinite dilution, placing the value for methyl iodide at 100, that for the others would be ethyl 10·37, propyl 4·38, octyl 3·01, cetyl 3·10. The action of potassium and sodium ethoxides on ethyl bromide also follows a law similar to the above with regard to concentration.

H. C.

Action of the Electric Arc on Gaseous Substances and its Employment for Demonstrations. By B. LEPSIUS (*Ber.*, 23, 1418—1428 and 1637—1642).—The author has successfully employed the apparatus described below for demonstrating the volumetric composition of various gases; its chief advantages over Hofmann's apparatus are that the experiments can be carried out in a comparatively short time, and a large volume of gas can be employed.



A glass tube A, 40 mm. in diameter and 300 mm. in length, is provided at its upper extremity with a glass stopcock, and, 40 mm. below the stopcock, with two lateral tubulures, 15 mm. in length and 15 mm. in diameter; it is closed below, but provided with a stopcock *a*, and an upright tube *b*, 10 mm. in diameter, as shown in the figure, the whole being placed on a suitable support. The

lateral tubulnres serve for the introduction of the carbon poles, which are about 2 mm. in diameter (or larger if required), and enclosed in metal necks, 12 mm. in length, which on the other side fit on to the pin (2 mm. in diameter) of a copper rod, 6 mm. in diameter, provided with a binding screw. The metal necks are made of iron or of brass (in the latter case they must be lacquered), and are slit down one side. The copper rods are fitted tightly into the lateral tubulures by means of indiarubber corks, and are of such a length that they overlap each other about 10 mm.; the corks being placed eccentrically in the tubulures in such a manner that the rods can be brought into contact by slight pressure on one of the binding screws. A current of 30 to 50 volts is sufficient to give the necessary arc, but it is better to employ a stronger current (60 to 80 volts) and a rheostat; the heat of the arc can then be regulated, so that the glass apparatus and the indiarubber corks are not damaged.

The gas is introduced in the usual way by first filling the apparatus with mercury.

The following examples serve to illustrate the use of the apparatus for lecture experiments:—*Conversion of Carbonic Anhydride into Carbonic Oxide.* Well dried carbonic anhydride (80—100 c.c.) is introduced into the apparatus, its volnme, measured under the atmospheric pressure, is marked on the tube, and the arc is ignited. Decomposition takes place with a brilliant light, and the volume immediately increases; in about a minute decomposition is complete, and after a short time the temperature is sufficiently equalised to allow of the measurement of the carbonic oxide, the volume of which is found to be double that of the carbonic anhydride employed.

Conversion of Oxygen into Carbonic Oxide.—Well dried oxygen (about 100 c.c.) is introduced into the apparatus, its volume is noted, and the arc is ignited; the volume increases continuously, and in one or two minutes the oxygen is completely converted into double its volume of carbonic oxide.

The volume relationship between oxygen, carbonic oxide, and carbonic anhydride can be very conveniently and quickly demonstrated with the following apparatus, a diagram of which is given in the original paper:—A glass tube A′, of the same size as the tube A, is provided at its upper extremity with a stopcock, and with two lateral tubulures through which pass two carbon rods, fitted exactly as shown in the figure, and described above, but instead of being closed below it is continued as a narrower tube (50 cm. long and 15 mm. in diameter), open below, the stopcock *a* and the upright tube *b* being done away with. The whole is filled with mercury, and suspended over a pulley in such a way that the open end dips into a deep, narrow, cylindrical depression in a mercury trough; this trough is supported on a small table, which can be moved up and down by means of a screw. The tube A′, the broader portion of which is marked off into six parts, each of 60 c.c. capacity, is now brought into such a position that the uppermost division is exactly opposite to a fixed pointer placed about 300—400 mm. above the level of the mercury in the trough, and 60 c.c. of oxygen are introduced; the arc is then ignited for about one minute, the apparatus is allowed to

cool, and the level of the mercury is again brought to that of the pointer, when it is seen that 120 c.c. of carbonic oxide have been produced. The tube A′ is again raised, so that the third division is opposite to the pointer, 60 c.c. of oxygen are introduced, and the tube is raised again as much as possible, in order to rarefy the gaseous mixture; the spark is then passed, and, after the explosion, the level of the mercury is brought opposite to the pointer, when it is seen that the three volumes have become two. The two volumes (120 c.c.) of carbonic anhydride thus produced can be converted into four volumes of carbonic oxide as already described, and then into four volumes of carbonic anhydride by explosion with two volumes of oxygen, the volume in both cases being shown by bringing the level of the mercury to that of the pointer; finally, the carbonic anhydride can be completely absorbed by introducing a small piece of moist potash. The apparatus and the oxygen employed must be free from moisture.

Conversion of Sulphurous Anhydride into Carbonic Oxide.—Dry sulphurous anhydride (about 80 c.c.) is introduced into the tube A shown in the figure, the volume is measured under the atmospheric pressure, and the arc is ignited; the carbon burns with a beautiful blue light, the apparatus becoming filled with white fumes, and the volume of the gas increases, and reaches a maximum in 30—40 seconds. On measuring the volume of carbon monoxide produced it is found to be double that of the sulphurous anhydride employed.

Formation and Decomposition of Sulphurous Anhydride.—Oxygen (80—100 c.c.) is introduced into the open tube A′, described above, the pointer being placed about 300 mm. above the level of the mercury in the trough, and then a piece of sulphur melted on to the end of a sharply-curved piece of copper wire is introduced from below, and ignited by momentarily closing the circuit. The sulphurous anhydride thus produced, the volume of which is equal to that of the oxygen employed, can then be converted into double the volume of carbonic oxide as described above.

That acetylene contains its own volume of hydrogen can also be demonstrated by means of the apparatus shown in the diagram.

The formation of water-gas can be very conveniently demonstrated by decomposing steam by means of the electric arc. For this purpose a flask, 15 to 20 cm. in diameter, is provided with two lateral tubulures, through which pass the carbon poles, arranged and adjusted as described above; the mouth of the flask is closed with a cork through which pass two glass conducting tubes, one reaching almost to the carbons, the other just passing through the cork; the flask is inverted on a stand, and steam is passed in through the longer tube. As soon as the air is completely expelled, the escaping steam is led under an inverted cylinder full of cold water; if, now, the arc is ignited, a rapid evolution of gas, consisting of equal volumes of hydrogen and carbonic oxide, is observed.

The same apparatus can be used for showing the formation of water-gas from water. The flask, provided with a single delivery-tube, is filled with water, placed in an upright position, and a strong current passed; the carbons become white hot, and a mixture of hydrogen and carbonic oxide is rapidly evolved. F. S. K.

A Lecture Experiment for the Demonstration of Valency. By B. LEPSIUS (*Ber.*, **23**, 1642—1646).—The apparatus described and shown in the preceding abstract can be employed for explaining experimentally the meaning of the term valency. Four such apparatus, 35 mm. in diameter, and 150, 200, 250, and 300 c.c. in capacity respectively, are so arranged that the uppermost stopcocks are all at the same level, and then filled with equal volumes (about 100 c.c.) of hydrogen iodide, hydrogen sulphide, hydrogen phosphide, and methane respectively, the volume being marked on the tube immediately after the introduction of the gas. The arc is then ignited in all the four apparatus, either separately or simultaneously, whereon the gases are quickly decomposed; after allowing to cool and adjusting the pressure the volume of the liberated hydrogen in the four tubes is seen to be in the ratio of 1 : 2 : 3 : 4.

All the gases must be as dry and pure as possible, and the apparatus containing the hydrogen iodide must be filled immediately before the experiment, but the others may be filled some time previously.

The hydrogen iodide is best obtained by heating an intimate mixture of melted phosphoric acid with double its weight of potassium iodide. The hydrogen phosphide is most conveniently prepared by the action of potash on phosphonium iodide. F. S. K.

Inorganic Chemistry.

Combustions under a High Pressure. By W. HEMPEL (*Ber.*, **23**, 1455—1460).—The author has carried out a large number of experiments in order to ascertain the influence of increased pressure on the quantity of sulphuric anhydride formed by the combustion of sulphur, and on the quantity of nitric acid produced by the combustion of nitrogen, either alone or with carbon.

The combustion of the sulphur was carried out in dry oxygen in iron vessels, that of the nitrogen in steel autoclaves lined with platinum; ignition was effected by means of a platiuum wire heated momentarily to its melting-point by an electric current.

Five quantitative experiments on the combustion of sulphur in oxygen showed that under a pressure of 40 to 50 atmos. about half the sulphur is directly oxidised to sulphuric anhydride; under a pressure of 72·5 atmos. the proportion of sulphuric anhydride produced is considerably less.

In the experiments on the combustion of nitrogen, varying quantities of air, oxygen, and electrolytic gas were compressed in an autoclave of 28 c.c. capacity, containing a little concentrated potash, and after combustion the nitric acid produced was reduced with ferrous

chloride, and estimated as nitric oxide; the results showed that the quantity of nitric oxide obtained increases with the pressure. When, for example, the autoclave is filled with air under the ordinary pressure, oxygen forced in until the pressure reaches 55 atmos., then electrolytic gas until a pressure of 211·5 atmos. is attained, a quantity of nitric acid corresponding to 10 c.c. of nitric oxide, is produced.

The nitric acid produced by the simultaneous combustion of nitrogen and carbon, in excess of oxygen, under various pressures was also determined; it was found that under a high pressure (88 atmos.), a very considerable quantity of nitrogen combines directly with the oxygen, but the quantity depends greatly on the relative weights of the two gases, and on that of the carbon employed.

The data of all the experiments are given in the paper.

F. S. K.

Formation of Nitrous Acid and Ammonia from free Nitrogen. By O. LOEW (*Ber.*, **23**, 1443—1447).—When dry platinum black, from which water dissolves neither nitrous acid nor ammonia, is shaken with soda, both nitrous acid and ammonia are formed; if the soda is very dilute the reactions of nitrous acid are obtained, but not those of ammonia.

The platinum black employed was most carefully prepared from platinic chloride free from nitric oxide, and the experiments were carried out in a room in which no fire or gas was burning, every precaution being taken to prevent contamination with nitrogenous compounds; the result was, however, always the same.

It would seem then that under the influence of the platinum black two processes take place:—(1.) The small quantity of nitrogen, condensed together with the oxygen in the platinum black, is directly oxidised to nitric oxide, which is then rapidly converted into nitrous acid. (2.) When concentrated soda is employed the nitrogen enters into reaction with the water as well, and ammonium nitrite is produced.

If air, purified by passing through concentrated sulphuric acid, concentrated potash, and several wash-bottles containing water, is conducted through a flask containing freshly prepared platinum black and a 0·5 per cent. solution (300 grams) of potash, the coloration produced with sulphanilic acid and α-naphthylamine, after acidifying with hydrochloric acid, is four times as intense after 12 hours as it was shortly after the commencement of the experiment, and the last wash-bottle does not contain a trace of nitrous acid. Large quantities of nitrite cannot, however, be obtained in this way, as the platinum black forms a compact layer at the bottom of the flask; better results would probably be obtained if the platinum black were allowed to condense a large volume of oxygen, containing nitrogen, by previous drying in the air.

A quantity of freshly prepared moist platinum black, corresponding to 23—24 grams of the dry substance, was mixed with about 5 grams of crystalline barium hydroxide, both substances being perfectly free from nitrous acid and ammonia, the mixture quickly washed on to a filter, kept for two days in a desiccator over calcium chloride, and

then washed with water (150 c.c.); the filtered washings gave a deep yellow colour with Nessler's reagent, and the total quantity of nitrous acid produced, estimated colorimetrically with Griess' reagent, was found to be about 0·7 milligram.

If active platinum black is treated with alcohol and then with chloroform, and finally placed in a desiccator over sulphuric acid for a day, it completely loses its power of causing the formation of nitrous acid and ammonia when it is shaken with air and soda, probably owing to the formation of a thin coating of platinum dichloride.

The fact that platinum at a high temperature causes the combination of oxygen and nitrogen, has been lately observed by Ilovsay (this vol., p. 447). This action commences at 180° with platinum black, at 250° with platinum sponge, and at 280° with platinum foil, but after prolonged heating at 300° the metal loses its activity.

The conversion of nitrogen into an assimilable form, at the ordinary temperature and without the aid of electricity, in the manner described above, is a fact of interest, on account of its bearing on vegetable physiology; because it may be assumed that an action which can be brought about by platinum black in presence of strong bases, can also be brought about by cells with an especially active protoplasm, even in presence of only a feeble alkali; the observations of Berthelot, Prantl, and Hellriegel and Wilfarth, on the fixation of atmospheric nitrogen by plants, seem to show that this assumption is well founded. F. S. K.

Combination of Phosphorus Pentafluoride with Nitrogen Peroxide. By E. TASSEL (*Compt. rend.*, **110**, 1264—1267).—When phosphorus pentafluoride is brought in contact with nitrogen peroxide at $-10°$, heat is developed, and a mass of white, elongated crystals, is formed, of the composition PF_5,NO_2. They dissociate even at the ordinary temperature and pressure, the dissociation being greatly accelerated by a slight rise of temperature; the products are phosphorus pentafluoride and nitrogen peroxide. Water decomposes the compound with formation of nitric and phosphoric acids and evolution of nitric oxide. Sulphuric acid dissolves it with liberation of phosphorus pentafluoride, whilst the nitrogen oxide remains in combination with the acid. C. H. B.

Action of Ammonia and Hydrogen Phosphide on the Haloïd Compounds of Arsenic. By BESSON (*Compt. rend.*, **110**, 1258—1261).—Arsenic trifluoride vapour acts on ammonia with formation of a very light, white powder, which, after being dried over sulphuric acid until it ceases to lose ammonia, has the composition $2AsF_3,5NH_3$. It is decomposed by water with formation of a feebly acid solution.

Arsenic trichloride at first absorbs ammonia very rapidly, but towards the end of the reaction the solid product must be repeatedly pulverised, and combination takes place very slowly. The compound formed is $AsCl_3,4NH_3$. Persoz attributed to this product the formula $AsCl_3,3NH_3$, and Rose the formula $2AsCl_3,7NH_3$.

Arsenic tribromide absorbs ammonia without alteration of its

crystalline form, and with formation of a straw-coloured compound, $AsBr_3,3NH_3$, which, in sealed tubes, decomposes at 300° with liberation of arsenic and nitrogen and formation of ammonium bromide.

Arsenic tri-iodide forms a pale yellow compound, $AsI_3,4NH_3$, which begins to lose ammonia at 50°, and at 300° decomposes in a manner similar to the bromide. Prolonged exposure to ammonia at 0° yields a yellow liquid of the composition $AsI_3,12NH_3$.

If the compound with arsenic chloride is added to cold concentrated sulphuric acid, energetic decomposition takes place, and drops of arsenic chloride separate in the liquid. The iodide compound behaves similarly with concentrated hydrochloric acid, arsenic iodide being liberated, and the author regards these reactions as evidence that these products are true molecular compounds.

Hydrogen phosphide forms no definite compounds with the haloid compounds of arsenic, but reacts energetically with them in accordance with the equation $PH_3 + AsX_3 = PAs + 3HX$, where X is a halogen. When the solid product is treated with water it yields a very light brown powder, $PAsO_3$, and small metallic-looking scales, $PAsO_6$, formed by the action of the water on the arsenic phosphide. The reaction between hydrogen phosphide and arsenic fluoride takes place at $-23°$, and with arsenic chloride at $-18°$. With the solid bromide and iodide the action is superficial, and phosphonium bromide and iodide are formed by the union of the haloid hydracid produced in the reaction with the excess of hydrogen phosphide. With the bromide melted at 30°, the reaction is very energetic.

C. H. B.

Arsenic Compounds. By K. PREIS (*Annalen*, **257**, 178—203; compare Abstr., 1888, 914).—When arsenic trioxide (1 mol.) is dissolved in a warm solution of sodium hydrosulphide (1 mol.), arsenic bisulphide is precipitated, and from the solution sodium oxythioarsenate, disodium arsenate, and a garnet-red salt, which seems to have the composition $4Na_2O,6As_2S_2,3As_2S_4O + 3H_2O$, can be isolated.

The following thioarsenates were prepared by precipitating a solution of sodium thioarsenate with a solution of the respective metallic salts:—$Hg_3(AsS_4)_2$, $Cu_3(AsS_4)_2$, and $Zn(AsS_4)_2$; the double salt, $NaZnAsS_4 + 4H_2O$, was also obtained in yellow crystals.

F. S. K.

Carbon Fluorides. By C. CHABRIÉ (*Compt. rend.*, **110**, 1202—1204).—Carbon tetrafluoride, prepared in tubes of Bohemian glass, contains only very minute quantities of silicon or carbonic anhydride, and its properties agree closely with those of the tetrafluoride prepared by Moissan in a metal vessel (this vol., p. 944).

Methylene fluoride, CH_2F_2, is obtained by heating 508 parts of anhydrous silver fluoride with 17 parts of methylene chloride at 180°. Analyses of the gas and its sp. gr. (1·82) show that it has the composition required by the formula. C. H. B.

Reduction of Alkaline Sulphates by Hydrogen and by Carbon. By BERTHELOT (*Compt. rend.*, **110**, 1106—1112).—The ordinary equation, representing the reduction of alkaline sulphates

by hydrogen, is not correct; some hydrogen sulphide is always evolved, and the residue contains some alkaline hydroxide. The reduction begins at about 500°, and the primary reaction is $K_2SO_4 + 4H_2 = KOH + KSH + 3H_2O$, which corresponds with a development of +2·6 Cal. in case of the potassium salt, and + 9·3 Cal. in the case of the sodium salt. Under the influence of the heat which is being supplied from the outside, the hydrosulphide dissociates with absorption of −9·5 Cal. for KSH, this change being accelerated by the current of water vapour and hydrogen. Part of the hydrogen sulphide escapes in the free state, and the rest acts on the potassium hydroxide, forming hydrosulphide and water with development of +12·8 Cal. The hydrosulphide continues to dissociate, and this change would convert all the potassium into monosulphide if some of the hydrogen sulphide were not carried away before there is time for the reaction to take place. Moreover, part of the monosulphide is decomposed by the water vapour, with formation of hydroxide and hydrosulphide, and development of +5·8 Cal. Between these various reactions, equilibrium is established, and is determined, as usual, by the presence of a dissociable compound, the hydrosulphide, and is governed by the tendency of the products to react with the development of heat on the one hand, on the other to dissociate with absorption of heat under the influence of the heat supplied from the outside. The water and hydrogen sulphide are carried away by the current of hydrogen, and thus the sulphate is completely reduced, the product being a mixture of sulphide and hydroxide in proportions determined by the conditions of the change. Some red potassium polysulphide is also formed as a result of the partial decomposition of the hydrogen sulphide into hydrogen and sulphur.

Reduction by Carbon.—Alkaline sulphates are reduced by carbonic oxide with formation of sulphide and carbonic anhydride, and development of +33·2 Cal. in the case of potassium, and +17·6 Cal. in the case of sodium. The change requires a much higher temperature than reduction by hydrogen, and does not take place below a bright red heat.

A mixture of a dry alkaline sulphate with pure carbon, in a vessel containing air, is reduced at about the same temperature as in the case of carbonic oxide, and the products are the same, carbonic anhydride being evolved, unless the carbon is present in very large excess. In complete absence of oxygen very little change takes place, even at bright redness, and the reduction observed is to be attributed to the formation of a small quantity of carbonic oxide by the action of the alkaline silicates formed from the porcelain of the tube. Under these conditions sodium sulphate alters more readily than the potassium salt.

The reduction of alkaline sulphates, on a large scale, by means of carbon in presence of air, takes place under the same conditions as reduction by carbonic oxide, and must be regarded as due to carbonic oxide. The presence of a small quantity of this gas is essential to the reduction; it is provided by the oxygen of the air in the vessel, the oxygen in the carbon, or by the oxides of the material of the

vessel. When once the reduction is in progress, the supply of carbonic oxide is furnished by the reaction; the carbonic oxide reduces the sulphate with formation of carbonic anhydride, and the latter is reconverted into carbonic oxide by the action of the excess of carbon.

It follows that in this case, as in others, carbon does not exert a direct reducing action, a result due to its polymeric constitution. In order that it may act as a reducing agent it must lose its state of condensation and be converted into a normal compound containing only one atom of carbon in the molecule.

In the reduction of salt cake, both carbonic oxide and hydrogen are active agents, the latter especially, when reduction is carried on in revolvers with the aid of gases from coal. C. H. B.

Silver Sub-Fluoride. By GUNTZ (*Compt. rend.*, **110**, 1337—1339).—When a saturated solution of silver fluoride is electrolysed with silver electrodes and a strong current, and the liquid is allowed to become hot, metallic silver is not deposited; but crystalline plates, with the colour of brass filings, separate at the cathode; they contain less fluorine than the normal fluoride, and when treated with water are decomposed into metallic silver and ordinary silver fluoride. The ratio of the silver dissolved as fluoride to the silver which separates in the metallic state is, practically, unity.

If finely-divided silver is heated with silver fluoride solution in a sealed tube, the liquid becomes yellow above 50°, and if the temperature does not exceed 90°, the whole of the silver is converted into the subfluoride Ag_2F, which forms a crystalline powder like brass filings. It is decomposed by water with development of heat.

$Ag_2Fl + nH_2O$ liquid $=$ AgF diss. $+$ Ag solid .... develops $+2{\cdot}73$ Cal.

hence—

Ag_2 sol. $+$ F gas $=$ Ag_2F solid .... „ $+24{\cdot}9$ „

and—

Ag sol. $+$ AgF sol. $=$ Ag_2F solid .... absorbs $-0{\cdot}7$ „

Silver subfluoride does not alter in dry air, and decomposes very slowly in moist air. C. H. B.

Phosphates of Lithium, Beryllium, Lead, and Uranium. By L. OUVRARD (*Compt. rend.*, **110**, 1333—1336).—The oxides or carbonates were dissolved in fused alkaline phosphates in the same way as in previous experiments (Abstr., 1888, 1033, 1035, 1037).

Lithium with any potassium phosphate, and with or without potassium chloride, yields only the compound $P_2O_5,3Li_2O$ in well-defined prisms which seem to belong to the rhombic system. Lithium carbonate and sodium metaphosphate yield the compound

$$2P_2O_5,3Li_2O,Na_2O$$

in small, flattened prisms which seem to be monoclinic; they are in-

soluble in water, but dissolve in acids. Sodium pyro- and ortho-phosphates yield the compound $P_2O_5,2Li_2O,Na_2O$ in imperfect crystals, or, if excess of lithium carbonate is added, the compound $P_2O_5,3Li_2O$.

Beryllium with potassium meta-, pyro-, or ortho-phosphate yields the salt $P_2O_5,2BeO,K_2O$ in rhombic prisms with an acute, positive bissectrix, the angle between the axes being about 30°. With sodium metaphosphate, Wallroth obtained the salt $P_2O_5,2BeO,Na_2O$ in hexagonal plates identical with the mineral beryllonite. The author confirms this statement, and has obtained the same compound by means of sodium pyrophosphate. Sodium chloride assists the formation of the crystals. Sodium orthophosphate yields a different product, $P_2O_5,BeO,2Na_2O$, in nacreous lamellæ with widely separated optical axes.

Lead.—Potassium metaphosphate yields lead pyrophosphate, $P_2O_5,2PbO$, free from alkali as colourless, transparent, rhombic prisms isomorphous with the corresponding barium and strontium componnds; they melt easily, and dissolve in dilute acids; sp. gr. at 20° = 5·8.

Potassium pyro- and ortho-phosphates yield the compound $P_2O_5,2PbO,K_2O$ in fusible, transparent, optically active needles, which are decomposed by boiling water. Sodinm metaphosphate at a dull red heat, with slow cooling, yields large, transparent lamellæ of the compound $9P_2O_5,10PbO,8Na_2O$. With a larger quantity of lead oxide at bright redness, the pyrophosphate $P_2O_5,2PbO$ is obtained. Sodium pyrophosphate yields the salt $P_2O_5,2PbO,Na_2O$ in small, brilliant, transparent prisms with oblique extinctions; they are readily fusible, and very soluble in dilute acids. Sodium chloride promotes the formation of the crystals, but if added in too large a proportion, causes the production of lead chlorophosphate. Sodium orthophosphate fuses at such a high temperature that no crystalline products could be obtained.

Uranium.—Potassium metaphosphate yields the pyrophosphate, P_2O_5,Ur_2O_3,K_2O, in transparent, yellow dichroic, highly birefractive, rhombic prisms of sp. gr. 4·2 at 20°. Crystallisation is promoted by the presence of potassium chloride. Potassium pyrophosphate yields highly birefractive, rhombic crystals of the phosphate $P_2O_5,2Ur_2O_3,K_2O$; potassium orthophosphate yields the salt $P_2O_5,Ur_2O_3,2K_2O$ in large, macled, yellow prisms. Sodium metaphosphate gives brilliant, sulphur-yellow, monoclinic prisms with oblique extinctions, their formation being promoted by the presence of sodium chloride. Sodium pyrophosphate dissolves large quantities of uranium oxide, and if not saturated gives products completely solnble in water. With a sufficient quantity of the oxide, the salt $P_2O_5,Ur_2O_3,2Na_2O$ is obtained in dendritic crystals. Sodium orthophosphate yields the same product mixed with a small quantity of sodium uranate.

No other metal has yielded a salt analogous to the compound $P_2O_5,Ur_2O_3,2K_2O$. C. H. B.

Dicalcium Phosphate. By H. CAUSSE (*J. Pharm.* [5], **21**, 544—547).—A phosphate, $Ca_2H_2P_2O_8 + 4H_2O$, crystallising in

rhomboidal forms is obtained by adding 500 c.c. of calcium chloride solution to 1500 c.c. of sodium phosphate solution saturated in the cold, then adding 100 c.c. of hydrochloric acid and some drops of sodium acetate. The salt contains P_2O_5, 41·40 per cent.; CaO, 32·65; and H_2O, 26·10. By the action of a solution of lactic acid on this phosphate, calcium dilactate and monocalcium phosphate are formed; the solution formed is only stable in presence of excess of acid.

J. T.

Thiosulphates. By A. Fock and K. Klüss (*Ber.*, **23**, 1753—1764).—*Potassium Cadmium Thiosulphates.*—(*a.*) $5K_2S_2O_3,3CdS_2O_3$. This salt is obtained by mixing equal volumes of concentrated solutions of potassium thiosulphate and cadmium acetate, and forms yellowish, monoclinic crystals; $a : b : c = 1·3203 : 1 : 0·95646$, $\beta = 87° 34'$. (*b.*) $3K_2S_2O_3,CdS_2O_3 + 2H_2O$, is prepared by employing a large excess of the potassium salt, and crystallises from warm water in beautiful, colourless, prismatic or tabular crystals, also belonging to the monoclinic system; $a : b : c = 1·5103 : 1 : 0·9631$, $\beta = 79° 21'$.

Sodium Cadmium Thiosulphates.—(*a.*) $3Na_2S_2O_3,CdS_2O_3 + 16H_2O$ is formed when an excess of sodium thiosulphate solution is added to one of cadmium acetate, and separates as an oil on the addition of alcohol. This solidifies over sulphuric acid in a vacuum to pale-yellow, transparent, tabular crystals, identical with those prepared by Jochum (*Inaug. Diss.*, *Berlin*, 1885). The crystals, which are very stable, are not deliquescent, and lose their water of crystallisation over sulphuric acid in a vacuum. They also crystallise in the monoclinic system; $a : b : c = 1·136 : 1 : 0·3492$, $\beta = 76° 25'$; (*b.*) $3Na_2S_2O_3,CdS_2O_3 + 3H_2O$ is obtained by avoiding an excess of the sodium salt. It forms yellow, prismatic, deliquescent crystals belonging to the triclinic system. They are not well developed, and the measurements are, therefore, inexact. The double salts described by Vortmann and Padberg, namely, $Na_2S_2O_3,2CdS_2O_3 + 7H_2O$ and $Na_2S_2O_3,3CdS_2O_3 + 9H_2O$, could not be obtained.

Ammonium Cadmium Thiosulphates.—(*a.*) $3(NH_4)_2S_2O_3,CdS_2O_3 + 3H_2O$ is formed by adding an excess of ammonium thiosulphate solution to a solution of cadmium acetate, and precipitating with alcohol; it is a white, crystalline salt, which separates from hot water in large, slightly yellow, tabular crystals belonging to the monoclinic system; $a : b : c = 0·9760 : 1 : 1·0026$, $\beta = 83° 45'$. It is stable in the air, but loses its water of crystallisation over sulphuric acid. (*b.*) $3(NH_4)_2S_2O_3,CdS_2O_3 + H_2O$ was obtained by mixing a solution of 1 mol. of cadmium acetate with 4 mols. of ammonium thiosulphate, and adding just sufficient alcohol to precipitate the yellowish oily liquid. On remaining over sulphuric acid, large rhombic tables separate; $a : b : c = 0·4317 : 1 : 0·4187$. (*c.*) $(NH_4)_2S_2O_3,CdS_2O_3$ is formed by mixing a solution of 2 mols. of cadmium acetate with one of 3 mols. of ammonium thiosulphate and adding absolute alcohol. On allowing the oil which separates to remain for some time under the mother liquor, it crystallises in large, yellow, monoclinic crystals;

$$a : b : c = 0·8216 : 1 : 1·5560, \beta = 82° 15'.$$

Barium Cadmium Thiosulphates.—(*a*.) $2BaS_2O_3,CdS_2O_3 + 8H_2O$ is prepared by digesting cadmium sulphate in aqueous solution with barium thiosulphate, and extracting the precipitate after some days with hot water. The salt separates in slender, yellow needles, sparingly soluble in water, belonging to the triclinic system; $a : b : c = 0·9871 : 1 : 0·8595$; $A = 79° 30'$, $B = 94° 15'$, $C = 57° 37'$, $\alpha = 80° 15'$, $\beta = 91° 37'$, $\gamma = 57° 50'$. (*b*.) $3BaS_2O_3,CdS_2O_3 + 8H_2O$ is formed when alcohol is added to the above hot water extract, the precipitate dissolved in hot water, and allowed to evaporate spontaneously. It forms yellowish triclinic tables or plates sparingly soluble in water; $a : b : c = 0·6997 : 1 : 0·6441$; $A = 94° 8'$, $B = 90° 30'$, $C = 79° 45'$, $\alpha = 94° 18'$, $\beta = 91° 18'$, $\gamma = 79° 11'$.

Strontium cadmium thiosulphate, $3SrS_2O_3,CdS_2O_3 + 10H_2O$, is obtained by adding alcohol to a mixture of concentrated solutions of strontium thiosulphate and cadmium acetate, and allowing the oil which separates to remain in a vacuum over sulphuric acid. It forms thick, yellowish, tabular crystals unsuitable for crystallographic examination, readily loses $5H_2O$ on remaining over sulphuric acid, and an additional 2 mols. on long-continued standing. A crystalline calcium cadmium thiosulphate could not be prepared. H. G. C.

Formation of Crystallised Metallic Oxychlorides: Copper Oxychlorides. By G. ROUSSEAU (*Compt. rend.*, **110**, 1261—1264).—The method used for preparing crystallised ferric oxychloride (this vol., p. 1063) is only available in the case of chlorides which are very soluble in water, or which form hydrates capable of aqueous fusion. Further, the decomposition of the dissolved chloride is possible only when the heat of formation of the chloride does not exceed that of the oxide by more than 4·8 Cal. The method is therefore applicable only in the case of tin, titanium, antimony, bismuth, magnesium, zinc, and iron.

Certain chlorides, cupric chloride, for example, seem to be exceptions to the second law, but in these cases the formation of the oxychloride is due, as Berthelot has shown, to its heat of hydration.

It is conceivable that in presence of a small quantity of water the hydrate of cupric chloride might dissociate more easily, giving rise to the formation of anhydrous chloride and the consequent production of new oxychlorides corresponding to special conditions of equilibrium. The hydrate $CuCl_2,2H_2O$ was heated with fragments of marble in sealed tubes at temperatures between 150° and 250°. A small quantity of an oxychloride was formed; this is readily decomposed by water, but can be isolated by dissolving the unaltered chloride in alcohol. It forms yellowish-green, hexagonal tables with oblique extinction, and the quantity formed in unit time increases with the temperature. It has the composition $CuCl_2,CuO,H_2O$, slowly loses its water above 250°, but retains its crystalline form, and is not decomposed. Below a dull red heat it melts to a black liquid, consisting of cupric chloride with the oxide in suspension.

If this oxychloride is treated with water, its colour changes to pale green, hydrochloric acid is liberated, and atacamite is formed. The oxychloride dehydrated at 300° also forms atacamite; when treated

with water, the substance seems to dissolve, but the atacamite is precipitated on the addition of a small quantity of an alkaline chloride.

The limit at which the oxychloride ceases to form lies between quantities of water corresponding with the formulæ $CuCl_2 + 4\frac{1}{2}H_2O$ and $CuCl_2 + 5H_2O$. Above the latter degree of dilution, atacamite is formed, and by heating a mixture of the composition $CuCl_2 + 6H_2O$ at 180—200° for three days, the author obtained atacamite in crystals identical with those of the natural mineral. Formation of the crystals takes place much more readily in presence of native magnesium carbonate than in presence of marble. A higher degree of dilution gives only amorphous products. C. H. B.

Action of Haloïd Compounds of the Alkalis on those of Mercury. By A. DITTE (*Compt. rend.*, **110**, 1330—1333).—The decomposition of a mercurous salt into a mercuric salt and mercury is eudothermic, and the combination of the mercuric salt with the excess of the haloïd salt is not sufficient to change the sign of the thermal disturbance. When mercurous chloride or bromide is treated with potassium iodide or cyanide, there is an interchange of acids and bases which determines a considerable development of heat, half the mercury being converted into mercnric iodide or mercuric cyanide, as the case may be. When mercurous iodide is treated with potassium cyanide, a similar exchange takes place, and the reaction is exothermic, but with potassium iodide the change remains endothermic. With potassium bromide and chloride, the reaction is endothermic with all the mercurous salts.

The occurrence of these endothermic decompositions is not appreciable at the ordinary temperature, but takes place more rapidly when the liquid is heated. Dilution of the liquid retards the change.

Mercurous salts are very slightly decomposed in presence of water alone, especially if the latter is heated, and in presence of a haloïd salt of an alkali metal, the mercuric salt produced will form a double salt. The formation of this double salt will destroy the equilibrium, and thus lead to a further decomposition of the mercurous salt. On the other hand, the double mercuric salt dissociates, especially if the solution is dilute, and a condition of equilibrium is established between the water, the mercurous salt, the double mercuric salt, and the products of their dissociation. If the solution is so dilute that the double mercuric salt is completely dissociated, the phenomena are the same as with pure water. A rise of temperature increases the dissociation of the mercurous salt and the double salt, but in presence of a sufficient excess of the alkaline haloid salt the double salt will be sufficiently stable to make the decomposition of the mercurous salt more rapid than at the ordinary temperature.

C. H. B.

Sodium Alum. By E. AUGÉ (*Compt. rend.*, **110**, 1139—1140).—The properties of sodium alum are very inaccurately described in all the books. It is only very slightly efflorescent, and may be kept for several months without alteration; 100 parts of water at 16° dissolve 51 parts of the salt. A solution of the alum can be boiled for any

length of time without losing the power of depositing the alum in crystals.

If a mixture of sodium and aluminium sulphate in proper proportions is concentrated without ebullition until its sp. gr. is higher than 38° Beaume, and is allowed to cool, it forms an amorphous paste, showing no trace of crystals even under the microscope, and this fact has probably given rise to the statement that the solution loses its power of crystallising. Temperature, however, has no influence in producing this result, for no matter how long the liquid is boiled, provided that its sp. gr. does not exceed 38° B., it readily deposits crystals; solutions above this degree of concentration always yield the amorphous product. If, however, the paste is allowed to remain at 7—25°, it gradually passes into crystals which have exactly the composition $Na_2Al_2(SO_4)_4 + 24H_2O$, the mother liquor being eliminated. Above 28°, crystallisation takes place very slowly; at temperatures approaching 0° hydrated sodium sulphate also separates. It is probable that the specimens of the alum which were observed to be efflorescent really contained a considerable quantity of sodium sulphate.

In the preparation of sodium alum, the mixture of the two sulphates should be concentrated to 39—43 B., and the paste should be placed on inclined lead plates so that as crystallisation takes place the mother liquor which separates, and which constitutes 25 per cent. of the paste, can readily run away, carrying almost all the impurities with it. C. H. B.

Composition of Clays and Kaolins. By G. Vogt (*Compt. rend.*, **110**, 1199—1202).—Clay cannot be separated by levigation from the very finely divided felspar, mica, or quartz with which it is mixed, since they all remain suspended in water for a long time. Mica being the only one of these minerals which sparkles when suspended in water, it may be concluded that clays which have this property contain mica, from which are derived the alkalis so often found in clays in a form soluble in sulphuric acid. When clays are treated with sulphuric acid, only the clay and the mica are dissolved; the felspar and quartz are not attacked. Both the solution and the insoluble matter will contain alkalis, that in the former (chiefly potassium) being derived from mica, and that in the latter from felspar.

C. H. B.

Manganous Acid. By A. Gorgeu (*Compt. rend.*, **110**, 1134—1137).—It seems almost impossible to obtain hydrated manganese dioxide containing the theoretical quantity of oxygen, but the pure dioxide is obtained in a crystalline, anhydrous form by heating manganous nitrate at 158—170°, or by the oxidation of manganite between 270° and 310°.

The best method of obtaining the dioxide in a form with strongly marked acidic properties is to bring together cold and dilute solutions of an alkaline permanganate and manganous nitrate in presence of a considerable quantity of free acid. The precipitate thus obtained is very finely divided, and is highly hydrated; it is manganous acid in its most active form.

The difficulty of preparing manganese dioxide from manganous oxide seems to be due to the fact that nitric acid and permanganic acid exercise a reducing action on manganous acid. Potassium manganite, obtained by the action of carbonic acid on the alkaline manganate, when boiled with nitric acid yields a residue containing distinctly less oxygen than manganous acid. The decomposition of permanganic acid at the ordinary temperature or at 100° yields a product containing 0·5 to 1·0 per cent. less of oxygen than the dioxide.

The hydrated peroxides differ in several respects from the anhydrous peroxides. They redden litmus-paper, and combine with soluble bases, forming manganites. The anhydrous peroxides show no acidic properties in contact with soluble bases, and many metallic salts, but if they are finely powdered and brought in contact with excess of manganous oxide, they will combine with 1·1 to 1·7 equivalents of it. The degree of hydration varies greatly even with different products obtained by the same method. All forms of the dioxide, whether anhydrous or hydrated, begin to decompose at the same temperature, about 400°.

When the hydrated forms of the dioxide are brought in contact with potassium or sodium hydroxide or ammonia, the quantity of alkali with which they combine increases with the concentration of the solution; in contact with lime-water or baryta-water, they combine with a relatively much higher quantity of the base than in the case of the alkalis. It would seem, therefore, that the quantity of the base which enters into combination depends on its solubility in water, or, in other words, on the tendency which its solution has to decompose the manganites which are formed. The acid function of the hydrated dioxide is sufficiently energetic to decompose soluble and insoluble carbonates and certain salts, such as acetates and even sulphates. The limits of the decomposition of salts seem to depend on their heat of formation; with potassium nitrate, manganite yields the compound $K_2O,25MnO_2$, and with sodium acetate, the compound $Na_2O,15MnO_2$. The composition of the compounds formed from the true metallic acetates and sulphates lies between the limits $K_2O,3MnO_2$ and $K_2O,9MnO_2$.

Potassium permanganate mixed with 20 per cent. of potassium hydroxide does not decompose even when boiled, but if manganous acid or, better, potassium manganite, $K_2O,5MnO_2$, is added, the precipitate gradually disappears at 100°, and the liquid becomes green without any evolution of oxygen. Potassium manganate is formed by the oxidation of the manganite by the permanganate, or by the combination of the permanganate with the bibasic manganite, $2K_2O,MnO_2$. This supposition would explain the failure to isolate manganic acid, and also the action of water and carbonic anhydride on a solution of a manganate. The dilution of the alkaline liquid or the neutralisation of the base would remove from the manganite the greater part of its alkali, thus preventing it from remaining in combination with the permanganate, and causing the precipitation of the acid potassium manganite. C. H. B.

Action of Hydrogen Peroxide on Permanganic Acid and Permanganates. By A. GORGEU (*Compt. rend.*, **110**, 958—961).—When a permanganate or permanganic acid is poured into hydrogen peroxide acidified with sulphuric acid, the manganese at once passes into the condition of manganese sulphate, with evolution of oxygen. A free acid is not essential, and any substance, like ammonium chloride, which can dissolve manganous oxide, will produce a similar result, provided that it is present in sufficiently large quantity.

When hydrogen peroxide is added to pure permanganic acid, the colour is gradually discharged, heat is developed, oxygen is liberated, and manganese peroxide is precipitated. The composition of the precipitate varies, but if the solutions are dilute, and the hydrogen peroxide is added very slowly to the permanganic acid, almost pure manganous anhydride, MnO_2, is formed. If the addition of the peroxide is continued after the liquid has been decolorised, the proportion of oxygen in the precipitate may be reduced by 17·9 to 13 per cent.

With an alkaline permanganate, the precipitate retains a considerable quantity of alkali, and a larger proportion of peroxide is required for complete decolorisation. A combination of manganese peroxide and the alkali seems to be formed, and reacts readily with the hydrogen peroxide. At first a brown solution is formed, which very readily decomposes, and which probably contains potassium manganite. In presence of a large excess of alkali, the brown liquid is not formed. The permanganate is first converted into the green manganate, and the latter is then decolorised.

If hydrogen peroxide is added to a neutral solution of barium permanganate, a brownish-yellow precipitate is formed, which contains all the barium, chiefly in the form of manganite, but with a small quantity of the manganate. If the permanganate is previously mixed with 2 to 4 equivalents of barium hydroxide in solution, all the barium is precipitated in the form of the deep blue manganate on addition of hydrogen peroxide. Excess of hydrogen peroxide exerts a powerful reducing action on the manganate and a feebler action on the manganite.

When hydrogen peroxide is added very slowly to a saturated aqueous solution of silver permanganate, a brown precipitate forms gradually until the liquid is decolorised. The reaction is represented by the equation $2AgMnO_4 + 3H_2O_2 = Ag_2O,2MnO_2 + 3H_2O + 3O_2$. The precipitated silver manganite is rapidly attacked by excess of hydrogen peroxide.

In all these cases the peroxide was added to the permanganate, and the quantity of peroxide decomposed varied from 3 to 11 equivalents per equivalent of permanganate. When the permanganate is added to the hydrogen peroxide, the quantity of the latter which can be decomposed is without limit. C. H. B.

Relative Basicity of the Hydrated Sesquioxides of Iron and Aluminium. By E. A. SCHNEIDER (*Annalen*, **257**, 359—380).—The author's experiments have confirmed the view at present held, that the hydrated sesquioxide of iron is a stronger base than that of

aluminium. When hydrated sesquioxide of aluminium is boiled with a dilute solution of ferric sulphate, the alumina does not play the part of a strong base, but simply neutralises a portion of the sulphuric acid, which is liberated by the dissociation of the iron salt, thus causing the precipitation of the whole of the iron as basic salt.

Solutions of the sulphate, chloride, and nitrate of aluminium of a certain concentration dissolve considerable quantities of ferric hydroxide. When water is added to such a solution of aluminium sulphate, in which ferric hydroxide has been dissolved, a basic iron salt is precipitated, but in the case of the aluminium chloride and nitrate solutions, the quantity of ferric hydroxide dissolved, provided it is present in excess, is increased considerably by the addition of water.

Ferric hydroxide can be readily converted into a colloidal modification which is soluble in water by treating it with a solution of aluminium chloride or aluminium nitrate.

Two modifications of aluminium hydroxide are obtained by precipitating aluminium salts with ammonia; the one dissolves in hydrochloric acid, yielding a solution which coagulates on the addition of a trace of sulphuric acid, but not in presence of excess of hydrochloric acid; the hydrochloric acid solution of the other modification is not coagulated on the addition of sulphuric acid.

F. S. K.

Crystallised Ferric Oxychloride. By G. ROUSSEAU (*Compt. rend.*, **110**, 1032—1035).—When solutions of ferric chloride, containing less than 80 per cent. of the salt, are heated in sealed tubes, only amorphous oxychlorides are obtained. With an 80 per cent. solution at 150—160°, traces of crystals of oxychloride are formed, but they dissolve readily in hydrochloric acid, and hence the formation of the oxychloride is limited by the hydrochloric acid set free at the same time. If the liquid contains fragments of marble or dolomite, a considerably larger quantity of the crystallised oxychloride is formed, but the amount never exceeds a few per cent. of the ferric chloride. As soon as the concentration of the solution falls below 80 per cent., amorphous products alone are obtained.

The crystals are red-brown, lustrous, rhombic prisms, of the composition $Fe_2Cl_6,Fe_2O_3,Fe_2(OH)_6$. In contact with hot water they lose all their chlorine as hydrochloric acid, and without loss of crystalline form pass into a ferric hydroxide, with the composition of göthite, the change being complete after 120 hours at 100°. The crystals of göthite have an amber colour, but retain the optical properties of the oxychloride, and therefore present a true case of isomorphism and not merely of pseudomorphism. The optical properties are not quite the same as those of the natural crystals of göthite, though both belong to the same system.

C. H. B.

Isomeric forms of Chromic Bromide. By A. RECOURA (*Compt. rend.*, **110**, 1029—1032 and 1193—1196).—*Green chromic bromide* was obtained by boiling a saturated solution of chromic acid with a large excess of hydrobromic acid and concentrating the liquid. It crystal-

lises in beautiful, green needles of the composition $Cr_2Br_6 + 12H_2O$, which deliquesce very rapidly and dissolve in less than half their weight of water at the ordinary temperature; heat of dissolution, +0·68 Cal. It is very soluble in alcohol but insoluble in ether.

While in the solid state, green chromic bromide undergoes no change, but it begins to alter as soon as it is dissolved, the solution becoming blue and finally violet, whilst a thermometer placed in the liquid readily shows the development of heat which accompanies the change. At the ordinary temperature, it requires several hours to complete the change, but this is accomplished very quickly if the liquid is heated. If the green solution is precipitated by an equivalent quantity of alkali and the hydroxide is at once dissolved in hydrobromic acid, the violet solution is obtained. The same form of the hydroxide is precipitated from both the green and the violet bromide.

The heat developed by the action of sodium hydroxide shows that the conversion of the dissolved green bromide into the dissolved violet bromide is accompanied by the development of +23·0 Cal.

A solution of 100 parts of green chromic bromide was boiled for a short time, then cooled and saturated with hydrogen bromide, the solution being kept cool throughout the operation. The fine precipitate which is suspended in the liquid is separated by filtration through glass wool, and dried on porous plates out of contact with moist air. It forms a blue-grey powder of the composition $Cr_2Br_6 + 12H_2O$, and is an isomeric modification of the green bromide. It is extremely hygroscopic and very soluble in water, forming a violet liquid. It differs from the green modification in being insoluble in alcohol; its heat of dissolution is +28·70 Cal., whilst that of the green form is only +1·36 Cal. It yields a violet solution which when treated with sodium hydroxide gives rise to exactly the same thermal disturbance as the violet solutions obtained from the green salt. It follows that the solutions of the blue bromide, the solutions formed by the spontaneous alteration of the green bromide, and the solution formed by the action of hydrobromic acid on the hydroxide precipitated from violet salts of chromium, are identical, and represent the definite stable condition of solutions of cupric bromide.

The conversion of the green bromide in solution into the blue bromide, also in solution, develops +23·0 Cal., but the conversion of the solid green bromide into the solid blue bromide absorbs −4·34 Cal. It follows that the green form is the more stable in the solid state, whilst the blue form is much the more stable in solution.

If the solid blue bromide is heated at 100°, it changes into the green form without loss of water, but the change either does not take place at all at the ordinary temperature, or takes place very slowly. In a moist condition and in contact with a solution of the green salt, the conversion of the blue solid salt becomes complete after several days, even at the ordinary temperature, the change probably being accelerated by the presence of some crystals of the green salt deposited from the mother liquor. When a solution of the blue bromide crystallises, the first crystals are blue, but those which form subsequently are green; a solution of the green salt deposits green crystals only. A solution of the green salt mixed with hydrobromic acid remains

green indefinitely, probably because the acid combines with the water and the bromide behaves as in a saturated solution.

The stability of the isomeric modifications of chromic bromide and their mutual conversions are in accord with the principle of maximum work. C. H. B.

New Double Chromates. By A. LACHAUD and C. LEPIERRE (*Compt. rend.*, **110**, 1035—1038).—When about 60 grams of lead chromate is added gradually in small quantities to 1,000 grams of fused potassium nitrate, and the mixture is heated for six or seven hours, three products are obtained, namely, (1) a brick-red, basic chromate, $PbCrO_4,PbO$, crystallising in the cubical system and insoluble in water; with acids it yields normal lead chromate and a lead salt of the acid; (2) a double chromate, $PbCrO_4,K_2CrO_4$, which crystallises in small, hexagonal plates, belonging to the rhombic system, and can also be obtained by adding a mixture of lead and potassium chromates to fused potassium nitrate; it is insoluble in hot or cold water and in alcohol, and is decomposed by acids with separation of lead chromate; (3) an orange compound, $PbCrO_4,K_2CrO_4,2PbO$, which crystallises in right rectangular prisms, and is formed more especially at a high temperature.

With sodium nitrate, the results are strictly analogous. The compound, $PbCrO_4,Na_2CrO_4$, however, crystallises in right prisms, and rarely has the appearance of hexagonal plates; it is soluble in water. The basic salt, $PbCrO_4,Na_2CrO_4,2PbO$, is obtained only in small quantity, and forms microscopic crystals belonging to the monoclinic system.

Lithium yields an analogous compound, $PbCrO_4,Li_2CrO_4$, which, however, is more readily obtained by the action of a very concentrated solution of lithium chromate on freshly precipitated lead chromate in sealed tubes at 140°. The ready decomposition of lithium nitrate interferes with the preparation of the salt in the same manner as in the case of potassium or sodium. The basic orange salt could not be obtained. C. H. B.

Electrical and Chemical Properties of Stannic Chloride. By W. COLDRIDGE (*Phil. Mag.* [5], **29**, 383—394 and 480—490).—Pure stannic chloride, heated as high as its boiling point, does not conduct electricity. The author in these papers investigates the effect of mixing foreign substances with the chloride, and discusses the whole question of electrolytic conductivity from the theoretical standpoint. Addition of chlorine had no effect on the conductivity, but dry hydrochloric acid permitted a small current to pass. Dry hydrogen sulphide had an electrical influence. It was observed, however, to precipitate white crystals from the chloride. These have the composition. $SnCl_4,5H_2S$, and are decomposed on heating, leaving a residue of SnS_2. Dumas's compound, $SnCl_4,SnS_2$, has no existence. Absolute alcohol forms white crystals with the chloride, probably $SnCl_4,5EtOH$, and these when dissolved conduct with facility, a stannous compound being formed and strong polarisation setting in. Ether behaves similarly to alcohol, forming a white, crystalline compound,

$SnCl_4,2Et_2O$, soluble in excess of ether and conducting well. Chloroform does not allow a current to pass. Concentrated aqueous hydrochloric acid, when mixed with the chloride, induces conduction and gives a considerable polarisation current. Insoluble solids have no effect when added to stannic chloride.

Taking these results into consideration, the author attributes electric conductivity to non-homogeneity of the electrolyte and consequent chemical exchange. J. W.

Action of Titanium Chloride on Metals. By L. LEVY (*Compt. rend.*, **110**, 1368—1370).—When vapour of titanium chloride is passed over silicon at a bright-red heat in an atmosphere of pure and dry hydrogen, very hard, steel-white, cubical crystals are obtained. Boron and many metals behave in the same way. Iron and antimony, however, cannot be used, and aluminium yields a mixture of the cubical crystals with hexagonal lamellæ of an alloy which has been described previously. The crystals are the same, whatever metal is employed; they have not the properties of titanium sesquioxide, and in all probability consist of almost pure titanium. They are not readily attacked by reagents, but are rapidly dissolved by fused potassium hydroxide with deflagration.

The crystals are cubes with the faces p, a', b', and are frequently macled, the hemitropic plane being one of the octahedral faces. C. H. B.

Complex Acids. By C. FRIEDHEIM (*Ber.*, **23**, 1505—1530; compare Rosenheim, Abstr., 1889, 762).—When vanadic anhydride is added to a boiling solution of acid sodium tungstate, the salt to which Rosenheim assigned the composition, $8Na_2O,16WO_3,4V_2O_5 + 57H_2O$, is deposited in crystals; the author's analyses of the carefully crystallised salt agree better with the formula $2Na_2O,4WO_3,V_2O_5 + 14H_2O$, and its chemical behaviour and its synthesis in the manner described below seem to show that it is a double salt of the composition $5Na_2O,12WO_3 + Na_2O,3V_2O_5$, and not a salt of a complex tungstovanadic acid. When sodium trivanadate is boiled with an equivalent quantity of acid sodium tungstate, it dissolves completely, and Rosenheim's is the only salt which can be obtained from the solution by crystallisation. Rosenheim's salt is also formed, together with various other compounds, when sodium metatungstate is boiled for some time with an equivalent quantity of normal sodium vanadate, and the solution then evaporated over sulphuric acid.

The mother liquors from Rosenheim's salt, prepared by the first method described above, contain a new double salt of the composition $4Na_2O,12WO_3,3V_2O_5$, and sodium metatungstate; on adding a cold saturated solution of barium chloride, and evaporating over sulphuric acid, a double salt of the composition $3(BaO,4WO_3) + BaO,3V_2O_5 + 30H_2O$ is deposited in ruby-red crystals, and on further concentration barium metatungstate separates from the solution.

The above results show that the reaction between acid sodium tungstate and vanadic acid may be expressed as follows:— $3(5Na_2O.12WO_3) + 6V_2O_5 = 2(5Na_2O,12WO_3 + Na_2O,3V_2O_5) + 3(Na_2O,4WO_3)$; on concentrating the solution, a small portion of the

acid sodium tungstotrivanadate thus produced is decomposed according to the equation $(5Na_2O,12WO_3 + Na_2O,3V_2O_5) + 3(Na_2O,4WO_3) = 3(Na_2O,4WO_3 + Na_2O.3V_2O_5) + 5Na_2O,12WO_3$.

Vanadic acid and acid potassium tungstate yield compounds analogous to those obtained with acid sodium tungstate, namely, the salt $2K_2O,4WO_3,V_2O_5 + 8H_2O$, and the salt $4K_2O,12WO_3,3V_2O_5 + 30H_2O$; the ammonium salts contain 3 and 30 mols. H_2O respectively The corresponding barium salts were also prepared.

Vanadic acid dissolves in a boiling solution of normal sodium tungstate; on evaporating over sulphuric acid, sodium sesquivanadate, $2Na_2O,3V_2O_5 + 15H_2O$, is deposited in large, reddish crystals, and the mother liquors on further concentration yield crystalline crusts of the double salt, $Na_2O,3WO_3 + Na_2O,2V_2O_5 + 20H_2O$.

Potassium sesquivanadate, $2K_2O,3V_2O_5 + 7H_2O$, was prepared in a similar manner.

The compound $3(Na_2O,2WO_3) + 2Na_2O,3V_2O_5 + 36H_2O$ is formed together with Rosenheim's salt when acid sodium tungstate is boiled with excess of normal sodium vanadate; when treated with acetic acid or boiled with tungstic acid, it is converted into Rosenheim's salt.

F. S. K.

The so-called Phosovanadic Acid and its Salts. By C. FRIEDHEIM and M. SZAMATÓLSKI (*Ber.*, **23**, 1530—1535).—Two series of double salts can be obtained by the combination of phosphoric and vanadic acid, namely, luteo- and purpureo-compounds. The former are yellowish, do not crystallise well, and are only sparingly soluble in, and are decomposed by, water.

Luteo-compounds.—The compound $P_2O_5,V_2O_5 + 11H_2O$ was obtained by treating vanadic acid with phosphoric acid, and the salts, $(NH_4)_2O,V_2O_5,P_2O_5 + 3H_2O$ and $K_2O,V_2O_5,P_2O_5 + 3H_2O$, $(NH_4)_2O,2V_2O_5,P_2O_5 + 7H_2O$ and $K_2O,2V_2O_5,P_2O_5 + 7H_2O$, were prepared, but several other compounds which have been described by Gibbs (*Amer. Chem. J.*, **7**, 209) and Ditte (*Compt. rend.*, **102**, 757) could not be obtained.

Purpureo-compounds.—The compounds of this class are deep-red, and are readily soluble. The potassium and ammonium salts have the composition $7R_2O.12V_2O_5,P_2O_5 + 26H_2O$, and crystallise well; the sodium salt was obtained as a vitreous mass. F. S. K.

Bismuth Potassium Iodides. By C. ASTRE (*Compt. rend.*, **110**, 1137—1139).—By the action of different proportions of potassium iodide on bismuth iodide, the author obtained three crystallised double salts:—$BiI_3,2KI$, which crystallises from ethyl acetate in brown, quadrangular lamellæ belonging to the quadratic system; $2BiI_3,3KI + 2H_2O$, which crystallises from ethyl acetate in groups of needles derived from a quadratic prism; and $BiI_3,3KI$, which crystallises from its aqueous solution, when the latter is allowed to evaporate spontaneously, in grey metallic crystals. This last salt crystallises from ethyl acetate in ruby-red, monoclinic lamellæ. C. H. B.

Chloro-Salts and Atomic Weight of Iridium. By A. JOLY (*Compt. rend.*, **110**, 1131—1134).—Iridium, which had been prepared

and especially purified by Deville and Debray, was converted into sodium iridiochloride by heating it with sodium chloride in a current of chlorine, and the potassium and ammonium salts were obtained by precipitation from a boiling solution.

The iridiochlorides were converted into the iridosochlorides by passing hydrogen sulphide into their boiling solutions until they acquired an olive-green colour and then adding an excess of alkaline chloride. *Potassium iridosochloride*, $IrCl_3,3KCl + H_2O$, forms large, deep-brown, quadratic crystals ($a : c :: 1 : 1·615$), olive-green in their sections by transmitted light. The ammonium salt, $IrCl_3,3NH_4Cl + H_2O$, forms olive-green or deep-brown, rhombic prisms of 98° 44′, $a : b : c :: 0·8581 : 1 : 0·4946$.

These salts lose all water at 120° and were reduced in hydrogen; three analyses of the potassium salt give Ir = 192·68 (H = 1), and two analyses of the ammonium salt give Ir = 192·82 (H = 1), the mean being Ir = 192·75, almost identical with the mean number 192·744 given by Seubert.

The action of nitric acid on iridiochlorides seems to yield a nitrosochloride, $IrCl_3(NO),2KCl$, analogous to the nitroso compound obtained from ruthenium under similar conditions. It forms soluble, vermilion-coloured crystals, which evolve nitrogen oxides at 440°.

C. H. B.

Iridium Phosphorus Chlorides. By G. GEISENHEIMER (*Compt. rend.*, **110**, 1004—1006).—One gram of hydrated iridium dioxide (this vol., p. 948) is heated in a sealed tube at 300° for 30 hours with 10 grams of phosphorus pentachloride and 15 grams of the trichloride. When all the oxide has dissolved the tube contains two layers of liquid; the heavier, which is garnet-red when hot, solidifies to a pale-yellow, crystalline mass when cold, the other contains excess of the chlorides of phosphorus and a double iridium phosphorus chloride, which crystallises on cooling.

The crystals are dissolved in phosphorus oxychloride in a sealed tube at 250°, and separate in pale-yellow crystals of the composition IrP_3Cl_{16}, which can be dried in dry air but have such a high tension of dissociation that they cannot be left in a vacuum, heated, or dissolved in any solvent which is not already perchlorinated.

If the crystals are heated gently to 70—80° and kept at this temperature for half an hour they yield the compound $Ir_2Cl_6,4PCl_3,2PCl_5$. At 120—125° the compound $Ir_2Cl_6,6PCl_3$ is formed. All three compounds have the same appearance, and are formed even in a current of chlorine. At 190° the compound $Ir_3P_6Cl_{20}$ is formed, but does not melt. If the temperature is raised rapidly instead of gradually to 150°, with reduction of pressure, the chloride melts, becomes very deep-red, loses phosphorus trichloride and pentachloride, and yields the compound $Ir_2Cl_6,2PCl_3,2PCl_5$ or $Ir_2Cl_6,2PCl_3,PCl_5$, according to the conditions.

Benzene reduces the original compound very rapidly; carbon bisulphide or phosphorus trichloride dissolves it readily but converts it into $Ir_2Cl_6,6PCl_3$. If heated with chloroform in a sealed tube at 160°, it is converted into small, red needles of the compound $Ir_2Cl_6,4PCl$.

It is rapidly attacked by water, and is completely dissolved if the compound is pure and the water is present in large excess; the solution when concentrated on the water-bath yields a syrupy, noncrystallisable acid, $Ir_2Cl_6,3H_3PO_3,3H_3PO_4$. If this is dissolved in a small quantity of water, and a large excess of alcohol added, it is thrown down in the form of a white, flocculent precipitate which rapidly agglomerates. The potassium salt, $Ir_2Cl_6,3PO_3H_2K,3PO_4H_2K$, is not crystallisable, dissolves in water, and is reduced by heat or by alcohol; the ammonium salt, $Ir_2Cl_6,3PO_3H(NH_4)_2,3PO_4(NH_4)_3$, is less easily reduced; the silver salt, $Ir_2Cl_6,3PO_3H_2Ag,3PO_4H_2Ag$, blackens when exposed to light and readily decomposes into silver chloride without precipitation of iridium; the lead salt, $2Ir_2Cl_6,6PO_3HPb,3(PO_4)_2Pb_3$, is white and insoluble in water or acetic acid but dissolves in nitric acid.

The compounds reduce ammoniacal silver nitrate, and with a solution of ammonium molybdate in hydrochloric acid they yield a yellow precipitate with a greenish tinge.

The compound $Ir_2Cl_6,6PCl_3$ is the easiest to prepare, and when pure and dry it is not attacked by cold water, but changes from yellow to white. After this alteration it dissolves slowly even in boiling water, and does not return to its original form even when heated at 125° in a current of chlorine or with chloroform in a sealed tube at 160°. When dissolved in water it yields a syrupy noncrystallisable acid, $Ir_2Cl_6,6PO_3H_3$; the potassium salt has the composition $Ir_2Cl_6,6PO_3H_2K$, and the lead salt $Ir_2Cl_6,6PO_3HPb$.

C. H. B.

Combination of Iridium Phosphochlorides with Arsenic Chloride. By G. GEISENHEIMER (*Compt. rend.*, **110**, 1336—1337).—Iridium phosphochloride (preceding abstract) dissolves easily in arsenic chloride, and if the solution is heated in a sealed tube at 250° and allowed to cool it becomes pale yellow and finally deep-red, and deposits ruby-red, prismatic crystals of the composition $2IrP_3Cl_{15},5AsCl_3$, which may be purified by washing with carbon bisulphide and drying in a current of air. The same product is obtained by heating hydrated iridium dioxide with arsenic trichloride and a very large excess of phosphorus pentachloride. It dissolves completely in water with liberation of hydrochloric acid, and if the solution is evaporated on a water-bath it yields the corresponding acid as a very deep-red, syrupy residue, which dissolves completely even in a very small quantity of water. The lead and potassium salts were prepared.

If, instead of an excess of phosphorus pentachloride, only so much is employed as will dissolve in the arsenic chloride, the product is the compound $IrCl_3,2PCl_3,2AsCl_3$, which crystallises in soft black needles with a violet lustre. They are insoluble in carbon tetrachloride, but dissolve in water yielding a violet solution.

C. H. B.

Mineralogical Chemistry.

Solubility of Minerals. By C. DÖLTER (*Monatsh.*, 11, 149—150).—The author has determined the solubility in distilled water, of minerals which are usually considered as insoluble. The following were used in the investigation:—Pyrites, galena, blende, antimonite, arsenical pyrites, bournonite, copper pyrites, tinstone, rutile, specular iron ore, heulandite, anorthite, natrolite, and chabasite. The samples, reduced to a fine powder, were placed in sealed tubes, and heated at 80° with distilled water for several weeks. All the minerals proved to be more or less soluble in water, the sulphides, rutile, and tinstone showing the greatest solubility.

The presence of sodium fluoride raises the solubility of rutile, tinstone, and specular iron ore, but sodium chloride does not produce a like effect. Carbonic anhydride increases the solubility of the oxides and sulphides; sodium sulphide and hydrogen sulphide that of the sulphides, especially antimonite. G. T. M.

Pyrargyrite from Kajénel in Transylvania. By H. TRAUBE (*Jahrb. f. Min.*, 1890, i, Mem., 286—289).—The crystals of pyrargyrite from Kajénel exhibit the following eight forms:—$\infty P2$, $\frac{\infty R}{2}$, $-\frac{1}{8}R$, $-\frac{1}{2}R$, $-\frac{3}{2}R$, $\frac{1}{4}R3$, $R2$, $-2R\frac{3}{2}$. Analysis of the mineral yielded the following results:—

Ag.	As.	Sb.	S.	Total.	Sp. gr.
60·45	1·02	20·66	17·87	100·00	5·76

B. H. B.

Tridymite and Chrystobalite. By E. MALLARD (*Compt. rend.*, 110, 964—967).—The crystals of silica from the Euganean hills, which von Lasaulx described as tridymite, have the form of tridymite crystals, but really consist of quartz into which the original tridymite seems to have been changed. This observation removes most of the doubt which existed as to the real properties of tridymite. The author has examined crystals of this mineral from Cerro San Cristobal and Mont Dore, and his results, combined with earlier observations, show that the crystals of tridymite are pseudo-hexagonal, but belong to the rhombic system with parameters $1 : \sqrt{3} : 1·629$ or $0·5774 : 1 : 0·9405$. The hexagonal plates are grouped in the same manner as aragonite; the mean index of refraction is 1·477, the acute positive bisectrix is normal to the plane 001, and the plane of the axes is normal to the ordinary axis of grouping. The change of state observed by Merian takes place at about 130°, is not accompanied by any considerable change of volume, and does not alter the crystalline form; it is therefore not a true change of the tridymite into quartz. It follows that, above 130°, silica can exist in two crystalline forms, with hexagonal symmetry and one optical axis, one of these forms being quartz and the other tridymite.

Chrystobalite is a distinct species and not merely a variety of tridymite. Its sp. gr., 2·34, is a little higher than that of tridymite, and it is somewhat easily attacked by alkalis. The crystals, which are usually imperfect, are pseudo-cubic, but really belong to the quadratic system. They are optically negative, and are grouped in such a way that the bases of six pyramids represent the six faces of a cube. The author has observed a similar grouping in analcime. Like the latter, chrystobalite is only approximately quadratic and uniaxial, and ought rather to be regarded as rhombic. At 175° it undergoes a reversible change, all birefraction disappears, and the crystals acquire the optical properties proper to their external cubical form.

C. H. B.

Crystallisation of Alumina and other Oxides in Gaseous Hydrogen Chloride. By P. HAUTEFEUILLE and A. PERREY (*Compt. rend.*, **110**, 1038).—At the ordinary pressure, hydrogen chloride has no action on alumina or zirconia at high temperatures nor on titanic anhydride at bright redness. Under a pressure of 3 atmos., however, and at a temperature below incipient redness, amorphous alumina is converted into corundum, titanic anhydride into anatase, and zirconia into rhombic tables. At the same temperature and under ordinary pressure, hydrogen chloride has a mineralising effect on the salts of these metals (carbonate, oxalates, sulphates), though not on the oxides.

The crystallisation of alumina is probably due to the successive formations and decompositions of a hydrochloride of alumina analogous to the hydrochloride of molybdic anhydride described by Debray, since under the conditions of the authors' experiments the decomposition of aluminium chloride yields amorphous alumina.

C. H. B.

Celestine from Mineral Co., West Virginia. By G. H. WILLIAMS (*Amer. J. Sci.* [3], **39**, 183—188).—Numerous crystals of celestine have recently been found in an extensive cutting on the line of the West Virginia Central Railway. They occur in an argillaceous limestone, and vary in colour from deep blue to colourless, and in length from less than a millimetre up to three inches. They are of pyramidal habit, which is not common for this species. This is due to the preponderance of the acute brachypinacoid $P\breve{4}$. Subjected to chemical examination, the crystals were found to be composed of strontium sulphate, with 0·12 per cent. of lime and a faint trace of barium oxide. These crystals acquire additional interest from their resemblance, in form as well as in their surface markings, to the well-known Sangerhausen pseudomorphs. B. H. B.

Phosphorites from the Government of Smolensk. By W. VERNADSKY (*Zeit. Kryst. Min.*, **17**, 628—629, from the Russian).—The principal mass of phosphorite occurs in green sands, rich in quartz, of Upper Cretaceous age. An analysis of a phosphorite nodule from Raditschi gave the following results:—

Ignition.	Insoluble.	P_2O_5.	CaO.	MgO.	Al_2O_3.	K_2O.	Na_2O.	S.
6·60	48·49	14·11	22·02	0·43	2·73	0·26	0·09	trace.

The nodules consist of wood and bones converted into phosphorite.

B. H. B.

Mineral Locality at Branchville. By G. J. BRUSH and E. S. DANA (*Amer. J. Sci.* [3], **39**, 201—216; and *Zeit. Kryst. Min.*, **18**, 7—23).—This is the fifth paper on this subject written by the authors. They now go on to a detailed account of some of the more interesting species discovered during recent developments at Branchville. Specimens have been obtained of all but one of the new species described in 1878. Besides these, the authors have found another new member of the triphylite-group, a sodium-manganese phosphate, which they term *natrophilite*, and another manganese phosphate, the rare mineral hureaulite, hitherto only known at Hureaux, in France.

Natrophilite occurs sparingly, usually closely associated with lithiophilite, with which it agrees in crystalline form. On analysis it yielded:—

P_2O_5.	MnO.	FeO.	Na_2O.	Li_2O.	H_2O.	Insol.	Total.	Sp. gr.
41·03	38·19	3·06	16·79	0·19	0·43	0·81	100·50	3·41

With the discovery of natrophilite, the triphylite-group receives an important addition, thus:

Triphylite	Li Fe PO_4,
Lithiophilite	Li Mn PO_4,
Natrophilite	Na Mn PO_4.

These three species are closely isomorphous.

The following analyses are also given:—

	P_2O_5.	FeO.	MnO.	CaO.	Na_2O.	K_2O.	Li_2O.
I.	38·36	4·56	42·29	0·94	—	—	—
II.	34·90	17·13	34·51	0·63	—	—	—
III.	(37·69)	3·42	17·40	30·02	—	—	—
IV.	40·89	12·96	31·83	2·09	7·37	1·80	0·22
V.	39·68	9·69	39·58	3·63	5·44	—	0·07

	H_2O.	Quartz.	Total.	Sp. gr.
I.	12·20	1·76	100·11	3·149
II.	13·18	0·13	100·48	3·204
III.	9·81	1·66	100·00	3·070
IV.	1·63	0·82	99·61	3·143
V.	1·58	1·02	100·69	—

I. Hureaulite in short, prismatic crystals; the analytical results agree with those obtained by Damour, and lead to the formula $H_2R_5(PO_4)_4 + 4H_2O$. II. Reddingite, formula $R_3(PO_4)_2 + 3H_2O$. III. Fairfieldite, formula $Ca_2Mn(PO_4)_2 + 2H_2O$. This analysis confirms the earlier one by Penfield. IV. Dickinsonite, formula $R_3(PO_4)_2 + \frac{1}{3}H_2O$. The results vary considerably from those of Penfield in his original analysis of impure material, the composition now established being essentially the same as that originally deduced for fillowite. V. Fillowite. The analytical results agree with the last, showing that the two species are essentially dimorphous forms of the same species.

B. H. B.

Phosphosiderite, a new Mineral. By W. BRUHNS and K. BUSZ (*Zeit. Kryst. Min.*, **17**, 555—560).—This new mineral, from the Kalterborn mine, near Eiserfeld, in the Siegen district, has a hardness of $3\frac{3}{4}$ and a sp. gr. of 2·76. It occurs in cavities in iron ore as a crystalline aggregate of a blood-red colour. Analysis gave the following results:—

Fe_2O_3.	P_2O_5.	H_2O.	Total.
44·30	38·85	17·26	100·41

Formula $(Fe_2O_3,P_2O_5)_2 + 7H_2O$. These results are very similar to those obtained by Nies on analysing strengite; formula, $(Fe_2O_3,P_2O_5)_2 + 8H_2O$. It therefore appeared not impossible for the two minerals to be identical. Whereas, however, in the mineral under examination all the water was given off at 140, strengite gave up its water at different temperatures; of the 8 mols., $1\frac{1}{2}$ being given up at 105°, and the remainder at 135°. The authors therefore propose the name of phosphosiderite for this new mineral. It crystallises in the rhombic system, the axial ratio being $a : b : c = 0·53302 : 1 : 0·87723$.

B. H. B.

Spangolite, a new Mineral. By S. L. PENFIELD (*Amer. J. Sci.* [3], **39**, 370—378).—A very beautifully crystallised specimen of an unknown mineral from Tombstone, Arizona, in the collection of N. Spang, proved to be a new species, a hydrated sulphate and chloride of copper. The crystallisation is hexagonal, rhombohedral, and the chemical composition of the mineral is as follows:—

SO_3.	Cl.	Al_2O_3.	CuO.	H_2O.	Total.	Sp. gr.
10·11	4·11	6·60	59·51	20·41	100·74	3·141

Its formula is $Cu_6AlClSO_{10},9H_2O$. There is at present no known mineral similar to this in composition. The rare mineral connellite, from Cornwall, is the nearest approach to it, in that this contains copper in combination with sulphuric and hydrochloric acids; but the form and properties of the two minerals are quite distinct. As far as can be found, these two minerals, together with sulphohalite, caracolite, and kainite, are the only mineral occurrences of sulphate and chloride in combination. The occurrence, too, of alumina in a copper mineral is very unusual. B. H. B.

Hornblende of St. Lawrence Co., New York. By G. H. WILLIAMS (*Amer. J. Sci.* [3], **39**, 352—358).—A perfect cross-parting due to intercalated twinning lamellæ, occurs on certain crystals of brown hornblende from Pierrepont, St. Lawrence Co. The phenomenon is analogous to the basal parting more commonly observed on pyroxene, and in view of the interest attaching to the structural planes of crystals the author has subjected these crystals to careful examination. From its composition. this hornblende is to be referred to actinolite. It presents two well-marked varieties: green (I) and brown (II), which, however, differ merely in colour. Analysis of these two varieties gave the following results:—

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.
I.	56·54	—	1·10	0·69	2·36	—	13·69	24·42
II.	56·44	0·11	1·77	0·84	0·73	0·11	11·83	22·98

	Na_2O.	K_2O.	Ignition.	Total.
I.	1·15	—	—	99·95
II.	2·13	0·75	2·46	100·15

Evidence afforded by thin sections of this mineral under the microscope shows that an alteration of the crystallographical symbols for the terminal planes of hornblende is necessary to show its analogy to pyroxene, on the assumption that the gliding plane, now called the orthodome $P\bar{\infty}$, is the basal pinacoid $0P$. B. H. B.

Production of Sillimanite: Constitution of Porcelain. By W. VERNADSKY (*Compt. rend.*, **110**, 1377—1380).—Sillimanite is the only aluminium silicate which has been produced artificially. Kyanite and andalusite change into sillimanite at 1350° with development of heat. Andalusite becomes white and opaque; in thin sections it extinguishes in a direction parallel with the prismatic edges of the original crystals, but the optical sign in the direction of elongation has become positive.

At a white heat an intimate mixture of finely-divided silica and alumina combines with development of heat, and fuses, forming a very hard, milky-white, slightly porous mass. After the heat of combination has been developed, and the mass has fused, it becomes solid, and will not melt again even in the hottest parts of a Leclercq and Forquignon furnace. A mixture of the composition $Al_2O_3 + 2SiO_2$ fuses well, but the reaction is less distinct with $Al_2O_3 + SiO_2$, though somewhat more distinct with $Al_2O_3 + 3SiO_2$.

The product consists of acicular crystals enclosed in an amorphous substance; the former act strongly on polarised light, and the optical sign in the direction of elongation is positive. The amorphous matter dissolves in cold hydrofluoric acid, but the crystals are not affected. They are, however, readily attacked at 70—80°. Crystals separated by means of the acid were found to have the composition Al_2O_3,SiO_2; the amorphous substance is almost pure silica, but contains small quantities of alumina. In presence of a small quantity of magnesium oxide, larger crystals of sillimanite are formed, but the magnesia does not enter into combination, and is easily removed by hydrofluoric acid, and even by strong hydrochloric acid.

As a general rule, when silica and alumina act on one another at a high temperature in absence of all but a small quantity of fixed bases, sillimanite is formed; this constitutes a large part of the products of the action of a high temperature on topaz, dumortierite, kaolin, and clays.

It is known that porcelain is a mixture of a crystallised and an amorphous substance, and thin plates have the same appearance as kaolin which has been heated at a high temperature. Treatment with cold hydrofluoric acid separates the crystalline from the amorphous matter slowly and with some difficulty, and the amorphous matter contains bases which form insoluble fluorides or silicofluorides.

Crystals separated in this way had the composition Al_2O_3, 70·3; SiO_2 29·7 per cent., which differs slightly from that of sillimanite. It is possible that excess of alumina adheres to the crystals, or a compound $11Al_2O_3,8SiO_2$ (Al_2O_3, 70·1; SiO_2, 29·9 per cent.) may be formed. In any case, porcelain consists of an amorphous substance and crystals which closely resemble sillimanite in composition. C. H. B.

Phonolites from Colorado. By W. Cross (*Jahrb. f. Min.*, 1890, 1, Ref., 427, from *Proc. Colorado Sci. Soc.*, 1887, 167—170).—In the United States hitherto but one occurrence of phonolite was known (Black Hills, Dakota). The author now describes a phonolite from a second locality near Florissant, Pasolty Co., Colorado. The rock is very similar in structure to that from Zittau. On analysis it yielded the following results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.
60·02	20·98	2·21	0·51	trace	1·18	trace	5·72	8·83

Cl.	P_2O_5.	H_2O.	Total.
trace	trace	0·70	100·15

Its sp. gr. is 2·576. The portion soluble in acid (25 per cent.) consists almost exclusively of nepheline. B. H. B.

New Swedish Minerals. By L. J. Igelström (*Jahrb. f. Min.*, 1890, **1**, Mem., 248—262).—1. *A New Mineral of the Olivine-group.*—A new variety of knebelite (magnesia-knebelite) has been discovered by the author at the Hilläng iron mine, in the parish of Ludvika, in the government of Dalekarlia. This mineral differs from the iron-knebelite, previously found by the author, in its pearly lustre and lighter colour. Besides which, it is invariably associated with small, red crystals of garnet, which never occur with the iron variety. An analysis of the new mineral gave the following results:—

SiO_2.	FeO.	MnO.	MgO.	Total.
31·1	42·6	21·6	4·7	100·0

The percentage of ferrous oxide must be too high on account of admixed grains of magnetite. The minerals belonging to the olivine-group, which contain iron and manganese in excess, have the following ratios between the iron and manganese-atoms:—

Fayalite	1 : 0
Knebelite	1 : 1
Iron-knebelite	2 : 1
Magnesia-knebelite	3 : 2
Eulysite-olivine	3 : 1
Tephroite	0 : 1

2. *Ferrostibian.*—This is a new mineral discovered by the author on July 13, 1889, at the Sjö mine, in the parish of Grythyttan, in the government of Örebro. The mineral is black, has a hardness of 4, and crystallises in the monoclinic system. Analysis gave the following results:—

SiO_2.	$(Mg,Ca)CO_3$.	Sb_2O_5.	FeO.	MnO.	H_2O.	Total.
2·24	2·14	14·80	22·60	46·97	10·34	99·09

Its formula is $(10RO,Sb_2O_5) + 10(RO,H_2O)$.

3. *Pleurasite.*—This is a new hydrated arsenate of manganese and iron from the Sjö mine. As yet it has only been qualitatively analysed. Its name is derived from πλευρᾶς (by the side), as it is found by the side of the arseniopleïte in bands of 1 cm. in thickness.

4. *Stibiatil.*—This is a new antimonate also from the Sjö mine. An approximative analysis yielded

FeO.	Mn_2O_3.	$Sb_2O_5 + H_2O$.	Total.
26	44	30	100

Stibiatil is thus a hydrated antimonate of manganese and iron, in which ferrous oxide is present in the greatest amount yet met with.

5. *Neotesite.*—This new mineral occurs in association with tephroite, pyrrhoarsenite, and calcite at the Sjö mine. On analysis it yielded the following results:—

SiO_2.	MnO.	FeO.	MgO.	H_2O.	Total.
29·50	40·60	trace	20·05	9·85	100·00

Formula: $(2RO,SiO_2) + H_2O$, in which RO represents MnO and MgO. As it is probable that this mineral was formed subsequently to the tephroite, the author terms it neotesite, from νεοτήσιος (young).

6. *Jacobsite and Braunite.*—The author has discovered these minerals in a new locality at Glakärn, in the parish of Linde, in the government of Örebro. Analysis shows the Glakärn jacobsite to have the same composition as that of Langban. B. H. B.

Garnet from the South African Diamond-fields. By E. COHEN (*Jahrb. f. Min*, 1890, 1, Ref., 393—394).—With the diamonds of South Africa, numerous garnets are found. In the dry diggings they are irregularly rounded grains, and in the river diggings they are uniformly rolled and polished. Analysis of wine-red (I) and deep hyacinth-red (II) garnets gave the following results:—

	SiO_2.	Al_2O_3.	Cr_2O_3.	FeO.	MnO.	CaO.	MgO.	Total.
I.	41·34	22·75	2·96	12·12	0·36	5·17	16·20	100·90
II.	40·90	22·81	1·48	13·34	0·38	4·70	16·43	100·04

Both these varieties, as well as the garnets of other shades of colour found at the Cape, are typical pyrope. B. H. B.

Syenites and Hornblende-schists near Glatz, in Lower Silesia. By H. TRAUBE (*Jahrb. f. Min.*, 1890, 1, Mem., 195—233).—The hornblende-bearing rocks of Glatz have been described, partly as of eruptive origin and partly as belonging to the crystalline schists. Microscopical investigation shows these rocks to have a similar mineralogical constitution, the component minerals being orthoclase, oligoclase, quartz, mica, and augite (hornblende). In all the rocks investigated, the hornblende is of secondary origin, having

been formed from augite. The structure of the two rocks, the syenites and the hornblende-schists of the geological maps, is very variable. The syenite may have a fibrous or slaty texture, and the hornblende-schist frequently resembles syenite. Analysis also shows that the composition is very similar. This similarity may be well seen from the following analytical results :—

	SiO_2.	Al_2O_3 + Fe_2O_3.	CaO.	MgO.
I.	66·07	19·89	3·86	2·04
II.	62·91	17·23	4·48	2·95

I is a partial analysis of the syenites of Follmersdorf, Werdeck, and Haunsdorf, a mixture being prepared of 20 grams of each of these rocks. II is a partial analysis of a similar mixture of the hornblende-schists of Maifritzdorf, Droschkau, and Werdeck. The differences exhibited in these two analyses are not greater than those occurring in each of the various rocks. It follows that a division of these rocks into syenites and hornblende-schist is not feasible. Both rocks have the same origin; they are intimately connected, and form a geological whole, which, in its mineralogical constitution and its structure, exhibits numerous variations. Whether these rocks should be classed as crystalline schists or as eruptive rocks. can only be determined by a careful geological survey. The contact-phenomena in the limestone at Neudeck render the latter hypothesis the more probable. The rocks may consequently be termed quartz-bearing augite-mica-syenites. B. H. B.

Minerals of the Syenite-pegmatite Veins of the South Norwegian Augite and Nepheline Syenites. By W. C. Brögger (*Zeit. Kryst. Min.*, **16**).—This memoir occupies 900 pages, and is illustrated by 38 figures, 27 lithographic plates, and 2 geological maps. Part I (pp. 1—100) is devoted to a summary of the geology of the Christiania district, with special reference to the eruptive rocks. Part II (pp. 101—235) is devoted to an account of the geology of the syenitic and nepheline-syenitic pegmatite veins of the coast between the Christiania fjord and the Langesund fjord. The remainder of the volume, the special part, contains a description of 73 minerals occurring in the syenite-pegmatite veins. In addition to the minerals previously known, the author has found iron-glance, nordenskiöldine, hambergite, xenotime, johnstrupite, epidote, calcio-thorite, datolite, muscovite, stilpnomelane (?), turmaline, diopside (and salite), lavenite, hiortdahlite, rosenbuschite, arfvedsonite. capelenite, melanocerite, karyocerite, soda-katapleïte, perovskite, eudidymite, thomsonite, weibyeite, and parisite. The number of well-defined mineral species known in the syenitic and nepheline-syenitic pegmatic veins occurring along the coast between the Christiania and Langesund fjords amounts to nearly 75, a number which renders this one of the richest mineral localities in the world. Of these 75 species, more than 20 have not been met with elsewhere, and 5 other rare species were first discovered here. The memoir contains a large number of important analyses. As many as 54 new analyses of minerals, and 43 new analyses of rocks have been specially made by

leading Swedish and Norwegian chemists. Space will not admit of all these analyses being reproduced, and it is not possible to do more than give brief descriptions of a few of the more interesting minerals described by the author.

1. *Nordenskiöldine*, named after the celebrated traveller, is of great rarity in the Norwegian veins. It crystallises in the rhombohedral-hemihedral system, and gave on analysis the following results:—

SnO_2.	ZrO_2.	CaO.	B_2O_3.	Ignition.	Total.
53·75	0·90	20·45	23·18	1·72	100·00

Formula, $CaSnB_2O_6$, or, less probably, $Ca(BO)_2SnO_4$. The crystallography of the mineral, however, indicates that it is a borate, and not a stannate. Its colour is yellow; its hardness 5·5 to 6; and its sp. gr. 4·20.

2. *Hambergite*, discovered by A. Hamberg in 1889, and named after him by the author, crystallises in the rhombic system. Its hardness is 7·5, and its sp. gr. 2·347. Analysis gave the following results:—

BeO.	H_2O.	B_2O_3.	Total.
53·25	10·03	36·72	100·00

Formula, $HO{\cdot}Be_2BO_3$. As a basic borate, this extremely rare mineral is one of the most interesting met with in the Norwegian veins.

3. *Xenotime*. This is a very pure yttrium phosphate, which, on analysis, gave results corresponding with the formula $Y_2(PO_4)_2$. In appearance this mineral differs from occurrences previously known by its deep brown colour, by its high sp. gr. of 4·62, and by its crystal form, $0P, P\infty$.

4. *Johnstrupite*, named after Professor F. Johnstrup, of Copenhagen, resembles mosandrite crystallographically and optically, but differs in colour, being green instead of brown. Analyses of mosandrite (I) and johnstrupite (II) gave the following results:—

	SiO_2.	TiO_2.	ZrO_2.	ThO_2.	CeO_2.	$Ca(LaDi)_2O_3$.	Y_2O_3.	Al_2O_3.
I.	30·71	5·33	7·43	0·34	6·34	10·45	3·52	—
II.	30·50	7·57	2·84	0·79	0·80	12·71	1·11	1·52

	Fe_2O_3.	MnO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	F.
I.	0·56	0·45	22·53	0·63	2·44	0·38	7·70	2·06
II.	0·50	trace	27·76	1·63	6·67	0·12	1·41	5·98

	Total.	Less O.	Total.
I.	100·87	0·86	100·01
II.	101·91	2·50	99·41

The two minerals present many points of similarity. Their differences are seen from the calculated formulæ:—

$$\text{Mosandrite}\ldots\ \left[\left.\begin{matrix}F_2\\(HO)_6\end{matrix}\right\}R_4^{iv}\right]R_2^{iii}R_{10}^{ii}(R_2^{i})_7[SiO_4]_{12}.$$

$$\text{Johnstrupite}\ldots\ \left[\begin{matrix}F_6R_3^{iv}\\F\ R^{iii}\end{matrix}\right]R_2^{iii}R_{13}^{ii}(R_2^{i})_4[SiO_4]_{12}.$$

5. *Calciothorite.* This mineral was discovered by the author a few years ago. It is amorphous, has a hardness of 4·5, and a sp. gr. of 4·114, and gave on analysis results corresponding with the formula $5(ThSiO_4),2(Ca_2SiO_4) + 10H_2O$.

6. *Astrophyllite.* From the results of a new analysis of this mineral, the author deduces the formula $R''_4R'_4Ti(SiO_4)_4$. He regards astrophyllite as a perfectly independent mineral not connected with the micas, nor with the minerals of the pyroxene group.

7. *Leucophane* and *Melinophane.* New analyses of leucophane (I) and meliuophaue (II) gave the following results:—

	SiO_2.	Al_2O_3.	BeO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O.
I.	48·50	0·45	10 03	0·27	22·94	12·42	—	1·08
II.	43·60	4·61	9·80	0·16	29·56	7·98	0·23	—

	F.	Total.	Less O.	Total.
I.	5·94	101·63	2·48	99·15
II.	5·43	101·37	2·27	99·68

From these results the following formulæ are deduced:—

I. Leucophane.. $Na_3(FBe)_3Ca_3(SiO_3)_6$ or $R_6'R_3''(SiO_3)_6$.
II. Melinophane. $Na_2(FBe)_2(Ca_2O)_2Be(SiO_3)_6$ or $R_4'R_4''(SiO_3)_6$.

8. *Wöhlerite.* A new analysis of this mineral gave the following results:—

SiO_2.	TiO_2.	ZrO_2.	Nb_2O_5.	Ce_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.
30·12	0·42	16·11	12·85	0·66	0·48	1·26	1·00	0·12	26·95

Na_2O.	H_2O.	F.	Total.	Less O.	Total.
7·50	0·74	2·98	101·19	1·24	99·95

9. *Rosenbuschite.* This mineral gave on analysis the following results:—

SiO_2.	$ZrOF_2$.	ZrO_2.	TiO_2.	Fe_2O_3.	Ce_2O_3.	MnO.	CaO.	Na_2O.	Total.
31·44	22·09	0·67	7·22	1·07	0·33	1·62	25·12	10·04	99·60

From these results the author deduces the formula

$$6CaSiO_3,2Na_2ZrO_2F_2,1Ti(SiO_3)(TiO_3).$$

Rosenbuschite, both in its crystal form and in its composition, presents sufficient analogies to pectolite for it to be described as a zircon-pectolite. An interesting result of this investigation of the Norwegian veins is the discovery of not merely three zircon-pyroxenes analogous to the ordinary pyroxene lengthened in the direction of the vertical axis, namely, lavenite, wöhlerite, and the asymmetrical hiortdahlite, but also of a zircon-pectolite, lengthened in the direction of the orthoaxis, corresponding with the pyroxenes of the wollastonite series.

10. *Karyocerite.* As this new mineral occurs in tablets of a nut-brown colour, the author has named it karyocerite, from κάρυον (nut),

and *cerium*, so as to indicate its relation to the black melanocerite. On analysis the mineral yielded—

SiO_2.	Ta_2O_5.	P_2O_5.	CO_2.	B_2O_3.	F.	ZrO_2.	CeO_2.	ThO_2.	Al_2O_3.
12·97	3·11	0·86	0·35	(4·70)	5·63	0·47	5·89	13·64	0·87

Fe_2O_3.	Mn_2O_3.	Ce_2O_3.	Di_2O_3.	La_2O_3.	Y_2O_3.	CaO.	MgO.	Na_2O.	H_2O.
1·36	0·66	14·83	6·75	14·34	2·21	7·37	0·17	1·42	4·77

Total.	Less O.	Total.
102·37	2·37	100·00

B. H. B.

Action of Solutions of Alkalis, Alkaline Earths, and certain Salts on Mica; Formation of Nepheline, Sodalite, Leucite, Orthoclase, and Anorthite. By C. FRIEDEL and G. FRIEDEL (*Compt. rend.*, **110**, 1170—1178).—The mica was heated at 500° with the various compounds and water in a steel tube lined with platinum for periods of 14 to 60 hours, according to the rate of change. The mica used was a Norwegian muscovite containing 7 per cent. of potassium oxide, and 3 per cent. of sodium oxide.

When the mica is heated with from 25 to 66 per cent. of potassium hydroxide, and not less than its own weight of water, it yields distinct brilliant, unmodified, hexagonal prisms. They are anhydrous. have the crystallographic properties of nepheline, and agree in composition with a mixture of 2 parts of soda nepheline and 1 part of potash nepheline. It is noteworthy that they contain an excess of soda, although formed in presence of an excess of potash. Fouqué and Michel-Levy have previously observed that it is not possible to obtain a pure potash nepheline in the dry way. When sodium hydroxide is used, the mica is more readily attacked, and the composition of the crystals corresponds with 3 parts of soda nepheline, and 1 part of potash nepheline.

If sodium chloride is also added in quantity varying from one-third to double the weight of the mica, sodalite is obtained in rhombic dodecahedra, modified by faces of the cube. It is identical in properties with the sodalite from Mt. Somma, and its composition is not materially affected by variations in the proportion of sodium chloride used. If, however, the quantity of salt is very little greater than that required to form sodalite, crystals of nepheline free from chlorine are obtained.

If the mica is heated with potassium silicate in the proportion required to form leucite, alteration takes place slowly, and well-formed crystals of orthoclase are obtained. If, however, it is heated with 50 per cent. of calcined silica, and 70 per cent. of potassium hydroxide for two days, the products are orthoclase, hexagonal, nepheline, and pseudo-cubic quadratic prisms, which have the composition and properties of leucite. The crystals are single prisms or macles of two or three prisms, in such a way that the quadratic axes become rectangular.

When heated with lime-water, mica yields small octahedral crystals of a hydrated aluminium calcium silicate, which seems to correspond with no known natural mineral. If calcium chloride is added in order

to decompose the sodium and potassium hydroxides, which must be liberated by the action of the lime, decomposition of the mica takes place readily, and the product forms almost rectangular lamellæ, more or less modified at the angles, which have the crystallographic properties of anorthite macles, and have the chemical properties of this mineral.

It is therefore possible to obtain from mica, by the action of aqueous solutions at a high temperature and under pressure, five minerals, nepheline, sodalite, orthoclase, leucite, and anorthite, which are fonnd in the eruptic rocks of Mt. Somma. C. H. B.

Some Secondary Minerals of the Amphibole and Pyroxene Groups. By W. Cross (*Amer. J. Sci.* [3], **39**, 359—370).—During the microscopical examination of some rocks from Custer Co., Colorado, the author observed two peculiar minerals of secondary origin, one an amphibole and the other a pyroxene. The former is a clear blue mineral occurring as a pseudomorphous replacement of common hornblende or of augite, with a pleochroism like that of glaucophane, whilst the orientation of the ellipsoïd of elasticity indicates that the mineral is closely related to the new species riebeckite. The pyroxene is bright green, and, although at first sight appearing to be orthorhombic in crystal form, is probably related to ægirite. The microscopical characteristics of these minerals are fully described. The results are of interest, inasmuch as, if the minerals in question are really ægirite and riebeckite, they appear in new associations, and were clearly formed under conditions quite different from those attending their origin in other known localities. B. H. B.

Meteoric Iron from North Carolina. By L. G. Eakins (*Amer. J. Sci.* [3], **39**, 395—396).—The iron described was found in 1880, on a farm near Ellenborough, Rutherford Co., and weighed originally about 2200 grams. In shape it has, roughly, two globular ends, with a connecting bar. The iron is very tough, and highly crystalline. Small irregular patches of troilite are visible, and schreibersite also seems to be present. Analysis of the iron yielded—

Fe.	Ni.	Co.	Cu.	P.	S.	Si.	Total.
88·05	10·37	0·68	0·04	0·21	0·08	0·02	99·45

B. H. B.

Mineral Waters of Malaisie: a Tin Mineral in Process of Formation. By S. Meunier (*Compt. rend.*, **110**, 1083—1085).—The water of Azer-Eanas, at Ulu Klang, which issues from the spring at a temperature of 50°, has a very peculiar and disagreeable odour, but evolves practically no gas when heated, and contains only 2 parts of inorganic matter in 100,000. On the other hand, it contains a large quantity of organic matter, which forms a syrupy residue when the water is evaporated.

The water of Azer-Panas, near Chevas, is quite different. It is hot when it issues from the spring, limpid, odourless, and has a very slight saline taste. When heated it becomes turbid, and evolves a large number of small bubbles of nitrogen. The water contains

chlorides, but no sulphates, and only traces of calcium; the total weight of sodium and calcium chlorides does not exceed 1·4 grams per litre.

The rocks at the spring of Azer-Panas are covered with greyish-white, earthy, vesicular concretions, of sp. gr. 2·1. They contain white, superposed scales, in which are small, black dendrites. The concretions are only slightly attacked by hydrochloric acid, even after several months. They contain SiO_2 91·8; H_2O 7·5; SnO_2 0·5; Fe_2O_3 0·2; Al_2O_3 traces = 100·0. The stannic oxide doubtless forms the black dendrites, and this is the first instance of a tin mineral in process of formation in a modern spring. C. H. B.

Organic Chemistry.

Melamine. By B. RATHKE (*Ber.*, **23**, 1675).—*Melamine*, $C_3N_3(NH_2)_3$, is obtained by heating pure melam, $C_6N_6(NH_2)_4{:}NH$, at 130°, with a 30 per cent. solution of ammonia; on evaporating to dryness and treating with water, the melamine dissolves; the residue consists of ammeline, which is simultaneously formed. J. B. T.

Synthesis of Ammeline and Cyanuric Acid. By E. BAMBERGER (*Ber.*, **23**, 1856—1869).—The formation of ammeline from dicyanodiamide and cyanic acid is explained by assuming that cyanoguanylcarbamide, $CN{\cdot}NH{\cdot}C(NH){\cdot}NH{\cdot}CO{\cdot}NH_2$, is first formed, and that, by the transference of a hydrogen-atom it changes spontaneously into the ammeline ring, $HN{<}{\begin{matrix}C(NH){\cdot}NH\\ CO{-\!-\!-}NH\end{matrix}}{>}C{:}NH$. This is in agreement with the conclusions of Smolka and Friedrich (compare this vol., p. 856), but not with those of Rathke (compare Abstr., 1886, 217), who refers all the additive properties of dicyanodiamide to the influence of the cyanide radicle, while the author assumes that this group only reacts in the case of compounds formed with water, hydrogen sulphide, and ammonia, the substances obtained by the addition of cyanic acid or thiocyanic acid being produced by interaction with the amido-group. The combination of carbonic anhydride and dicyanodiamide to form melanurenic acid, $NH{<}{\begin{matrix}CO{\cdot}NH\\ CO{\cdot}NH\end{matrix}}{>}C{:}NH$, also belongs to the second class. In a similar manner, the reactions of cyanamide may be separated into two divisions; accordingly the compound obtained from cyanamide and cyanic acid should be represented as cyanocarbamide, $NH_2CO{\cdot}NH{\cdot}CN$, and not as amidodicyanic acid, $CO{<}{\begin{matrix}NH\\ NH\end{matrix}}{>}C{:}NH$, as hitherto; its properties, and formation from dicyanodiamide by the action of barium hydroxide, being in agreement with this theory. The polymerisation of cyanoamide to form dicyanodiamide may be represented as being strictly analogous to the

aldol condensation, and to the formation of imidoacetyl methyl cyanide from methyl cyanide; the same relation is observed during the further changes into cyanoacetone and cyanocarbamide (amidodicyanic acid) respectively. In a similar manner, melamine,

$$NH<\begin{matrix}C(NH)\cdot NH\\C(NH)\cdot NH\end{matrix}>C:NH,$$

is produced from dicyanodiamide by a second condensation with cyanamide, the hypothetical intermediate product being cyanobiguanide, $NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH\cdot CN$.

In addition to the methods already known, ammeline may be prepared by heating dicyanodiamide with finely powdered, anhydrous potassium cyanate, at 200—205°, for about 20 minutes; when cold, the product is dissolved in boiling water containing a little sodium hydroxide, and the ammeline precipitated with acetic acid. On evaporation of the mother liquor, a second portion of ammeline is obtained; this is removed, and the liquid further concentrated and treated with dilute sulphuric acid, when crystals of melamine sulphate separate; the yield of ammeline is 100 per cent. of the dicyanodiamide employed.

Cyanuric acid may be prepared by heating together equal parts of biuret and ethyl carbamate for two hours at 160—170°; a considerable evolution of ammonia occurs, and the product when dissolved in hot water, yields pure cyanuric acid on cooling. Potassium cyanurate is obtained on substituting potassium cyanate for the ethyl carbamate in the above reaction. For this purpose a mixture of biuret with potassium cyanate in molecular proportion is heated at 130°; the reaction is somewhat violent; the potassium salt crystallises out on treating the product with hot water.

These syntheses of cyanuric acid are represented as being completely analogous to the formation of ammeline, and, in the author's opinion, they afford a further proof of the correctness of this condensation theory. J. B. T.

Stereochemistry of Ethane Derivatives. By K. AUWERS and V. MEYER (*Ber.*, **23**, 2079—2083).—The recent researches of Bethmann, Graebe, and Baeyer have confirmed the conclusion previously arrived at by the authors, namely, that in certain compounds the singly-bound carbon atoms are not capable of free rotation.

The results obtained by Bethmann and Graebe seem to indicate that Wislicenus' theory as to the free rotation of singly-bound carbon atoms must be limited to certain cases; absolutely free rotation is probably possible only when the substituting atoms or groups are identical; where, as is the case in the majority of compounds, the atoms or groups are not identical, there will be some definite position of equilibrium; only in cases where the substituting atoms or groups are equally negative will there be several positions of equilibrium.

F. S. K.

Constitution of α-Dibromhydrin. By O. ASCHAN (*Ber.*, **23**, 1826—1831).—α-Dibromhydrin yields bromodinitromethane and bromacetic acid on oxidation with nitric acid of sp. gr. 1·48.

α-Dichlorhydrin gives the corresponding chlorinated-compounds.

α-Dibromopropyl acetate is prepared by heating α-dibromhydrin with acetic anhydride at 120°; it is a colourless strongly refractive liquid, of sp. gr. 1·8248 at 16°; it boils at 227—228°, and undergoes decomposition on exposure to light. *αβ-Dibromopropyl acetate* is obtained in a manner similar to the α-compound, which it closely resembles; it boils at 227—228°, and has a sp. gr. of 1·8281 at 16°. The author considers that his results prove the correctness of the generally accepted formula for α-dibromohydrin. J. B. T.

Atomic Re-arrangement of Allyl Compounds. By O. ASCHAN (*Ber.*, **23**, 1831—1839).—α-Dibromhydrin, on distillation, decomposes into epibromhydrin, allyl aldehyde, and hydrobromic acid. Allyl alcohol and epibromhydrin are formed by the action of sodium on α-dibromhydrin or α-dibromopropyl acetate. The author explains these observations by assuming that the changes take place according to the following equations:—

$$CH_2Br\cdot CH(OH)\cdot CH_2Br + Na = CH_2Br\cdot CH<\genfrac{}{}{0pt}{}{O}{CH_2} + NaBr + H.$$

The remaining atom of bromine is then eliminated in a similar manner by the action of a second atom of sodium, giving the compound $CH_2{:}C<\genfrac{}{}{0pt}{}{O}{CH_2}$, from which allyl aldehyde, $CH_2{:}CH\cdot CHO$, is formed by re-arrangement, and this is then reduced to allyl alcohol by the hydrogen liberated in the previous stages. J. B. T.

Greater or Less Rotation (Multi-Rotation) of Sugars. By E. PARCUS and B. TOLLENS (*Annalen*, **257**, 160—178).—The authors propose to employ the term "multi-rotation" to denote the change (increase or decrease) of rotatory power which takes place in a sugar solution, from immediately after its preparation in the cold until constant rotation is attained; a sugar solution, the rotatory power of which increases on keeping, may be said to show "greater rotation," when the opposite is the case "less rotation."

A number of sugars have been examined in order to obtain more exact knowledge of the phenomenon of multi-rotation, special pains having been taken to determine the rotatory power as soon as possible after solution; the observations were made at 20°, and the solutions employed contained about 10 per cent. of the sugar. From the data thus obtained the authors have, in the case of each sugar, constructed a curve, the ordinates representing the change of rotation, the abscissæ the time that has elapsed since solution; the form of the curves is, generally speaking, very regular, and the values obtained for constant rotation agree very well on the whole with those obtained by previous investigators. The experiments also show that dextrose is the only sugar that shows bi-rotation; in the case of xylose, the proportion between the initial and the constant specific rotatory power is rather more than 4 : 1, whilst in the case of arabinose and lactose it is about 8 : 5. Galactose, maltose, and levulose were also examined.

F. S. K.

Melitriose and Melibiose. By C. SCHEIBLER and H. MITTELMEIER (*Ber.*, **23**, 1438—1443; compare this vol., p. 226).—In the preparation of melibiose by the hydrolysis of melitriose with sulphuric acid, the authors have observed that in extracting the concentrated syrup, previously freed from acid, with absolute alcohol, not only levulose, but also considerable quantities of melibiose, pass into solution; on cooling, however, the alcoholic extracts deposit the greater portion of the melibiose as a colourless powder, free from levulose.

Anhydrous, amorphous melibiose has the composition $C_{12}H_{22}O_{11}$, and its specific rotatory power was found to be $[\alpha]_D = 126\cdot8°$ as a mean of two determinations.

Melibiosephenylhydrazine, $C_{18}H_{28}O_{10}N$, forms yellow, microscopic crystals, melts at 145°, decomposes at 160°, and is readily soluble in water, but only sparingly in alcohol, and insoluble in ether, benzene, and chloroform; when warmed with an aqueous solution of phenylhydrazine acetate, it yields phenylmelibiosozone.

Octacetylmelibiose, $C_{12}H_{14}O_{11}Ac_8$, prepared by boiling melibiose with acetic anhydride and sodium acetate, crystallises from hot alcohol in small needles, melts at 170—171°, and has a very bitter taste. It is almost insoluble in cold water, and only sparingly soluble in carbon bisulphide, light petroleum, and hot water, but readily in chloroform, hot alcohol, glacial acetic acid, and benzene. Its specific rotatory power is $[\alpha]_D = 94\cdot2°$. It reduces Fehling's solution on warming, and dissolves unchanged in phenylhydrazine.

Undecylacetylmelitriose, $C_{18}H_{21}O_{16}Ac_{11}$, is formed when melitriose is boiled with acetic anhydride and sodium acetate. It separates from alcohol very slowly in small crystals, has a bitter taste, and is readily soluble in alcohol, ether, phenylhydrazine, aniline, chloroform, benzene, and glacial acetic acid, but only sparingly in carbon bisulphide and light petroleum. It melts at 99—101°, does not reduce Fehling's solution, and its specific rotatory power is $[\alpha]_D = 92\cdot2°$.

F. S. K.

Carbohydrates. By A. WOHL (*Ber.*, **23**, 2084—2110).—In investigating the inversion of sugar by hydrofluoric acid, the author found that the inversion in concentrated solutions is the more complete, that is to say, the maximum levo-rotation is the greater, the smaller the quantity of acid employed. This is also true in the case of other mineral acids, and it was found that for each acid there is, within narrow limits, a certain concentration which is dependent on the conditions of the experiment whereby sugar, even in 80 per cent. solution, can be almost completely inverted, and the formation of decomposition products minimised. By heating pure cane-sugar (80 parts) with water (20 parts) containing only 0·004 part of hydrochloric acid for an hour at 95—100°, a colourless solution of pure inverted sugar (84 parts) is obtained.

Experiments were then commenced in order to ascertain the cause of the seemingly incomplete inversion of sugar in concentrated solutions. For this purpose, cane-sugar (13·024 grams) was heated at 100° for half an hour with 0·04 per cent. hydrochloric acid (3·3 c.c.), in a closed flask, the solution being then diluted to 100 c.c., kept for 24 hours, and examined in a saccharimeter (200 mm. in length), at a

temperature of 20°; the observed polarisation was −12·0°, from which the quantity of sugar inverted is calculated to be about 95 per cent., whilst estimations by Allihn's method gave 96 per cent. If the solution is heated for more than half an hour, both its polarisation and its reducing power are diminished; after an hour's heating, for example, the polarisation is −10·5°, after two hours, only −9·0°, and in the last case the solution turns yellow. The rotatory and reducing power are also diminished when the concentration of the sugar solution or the quantity of acid employed is increased. This decrease of levo-rotatory power is due to the fact that the inverted sugar, formed in concentrated solutions, is, partially at least, chemically different from that obtained by the inversion of dilute solutions; that this difference is not caused by a partial decomposition of the levulose was proved by special experiments, so that it can only be due to incomplete inversion, or to a condensation of the inverted sugar similar to that observed by Degner, or to a combination of the two phenomena.

Further experiments proved that a solution of pure inverted sugar, prepared from pure levulose and pure dextrose, shows the same behaviour with hydrochloric acid as the solution of inverted sugar obtained from cane-sugar, and, therefore, the diminution in rotatory and reducing power is in both cases due to the same cause; it was also found that the condensation of inverted sugar is principally the effect of the action of the acid, not of that of the water.

It follows, therefore, that the inversion of sugar in concentrated solutions is not really incomplete, but is accompanied by a condensation process of an opposite kind, brought about by the acid employed.

When a concentrated solution of dextrose is heated with a small quantity of hydrochloric acid under conditions similar to those employed in the case of the inverted sugar, no appreciable effect is produced, but the rotatory and reducing power of a solution of levulose are considerably diminished, and to about the same extent as is the case with a solution of inverted sugar; hence the condensation of inverted sugar is a condensation of levulose alone.

When levulose (13·7 grams) is heated at 100° for an hour with 0·136 per cent. hydrochloric acid (0·25 c.c.), the mixture then dissolved in warm alcohol (50 c.c.). and kept for 12 hours, a dextrin-like substance is deposited which, after having been washed with cold, and redissolved in warm, alcohol, is obtained as a colourless, very hygroscopic powder. The rotatory power of this substance is about one-half, and its reducing power less than one-third that of levulose; it is probably a mixture of various dehydration products, and when its dilute solution is heated with hydrochloric acid it is slowly reconverted into levulose.

Dextrin-like products are also formed when an 80 per cent. solution of dextrose is heated at 105° with moderately concentrated (0·05 to 1·0 per cent.) hydrochloric acid.

The above experiments prove that the hydrolytic decomposition of di- and poly-saccharoses is not a simple change, but that the inverting action of the acid is accompanied by a reverting action, which transforms the simple glucoses into dextrin-like substances.

When sugar, in 80 per cent. aqueous solution, is heated at 100° with 0·005 per cent. of hydrochloric acid, the maximum levo-rotation (−12·35°) is attained in about 35 minutes, the solution being then perfectly colourless; on further heating, however, the rotation gradually diminishes, and after two hours from the commencement of the experiment it is only −10·15°, and the solution has become distinctly yellow. The maximum levo-rotation, which corresponds very closely with the maximum reducing power, shows the point at which the subsequent inversion in the unit of time is exactly counterbalanced by the reversion which takes place. It is not, therefore, the point of complete inversion in the sense that no unchanged sugar remains, although the quantity of the latter, under the dominating conditions, is extremely small; the apparent inversion at this point, ascertained by estimating the reducing power, is 95·8 per cent., but as that portion of the inverted sugar which has already undergone reversion, has a far smaller reducing power than that which has not, the quantity of changed and unchanged inverted sugar together, must be considerably greater than appears from the reducing power, and the quantity of cane-sugar correspondingly less. Considering also that the reducing power of a solution of a mixture of equal parts of pure levulose and pure dextrose undergoes approximately the same diminution in the same time, there can be only an extremely small quantity of reverted sugar present in the above solution. That the reversion has not proceeded very far, and that the product thereof is closely allied to levulose is also proved by the fact that the concentrated solution is almost colourless, and that on subsequent inversion in dilute solution it attains almost the theoretical levo-rotation.

The maximum levo-rotation, either of a dilute or concentrated solution, shows, therefore, the point of relatively most complete inversion, that is to say, at this point the quantity of unchanged inverted sugar has reached its maximum for the degree of concentration in question.

Since then it has been shown that decomposition does not necessarily accompany the inversion of concentrated sugar solutions by mineral acids, but is simply the effect due to excess of acid being used; if such excess is avoided by adjusting the quantity of acid according to the percentage of ash contained in the sugar, the completeness of inversion will no longer be dependent on any particular concentration of the solution. That this has not been previously observed is probably due to the fact that in the case of hydrochloric acid—the acid which is most used for inversion experiments—the quantity which is exactly requisite is very nearly the same as the quantity which is just within the extreme limit permissible. For example, in order to convert pure sugar into colourless, inverted sugar, by heating its solution for half an hour at 95°, the amount of hydrochloric acid employed should be, at the most, 0·01 per cent. of the sugar; if the quantity is below the limit, the inversion is greatly and disproportionately retarded, and if the limit is exceeded, the solution quickly turns yellow, and the product is useless.

Preparation of Levulose.—A very small quantity (0·01 per cent.) of hydrochloric acid is sufficient to convert pure inulin, free from ash, into

levulose; in the case of inulin that contains up to 0·2 per cent. of ash, the percentage of acid employed is about one-half the percentage of ash; when the ash amounts to 0·2 to 0·4 per cent., the percentage of hydrochloric acid is about two-fifths the percentage of ash; further purification of commercial inulin is unnecessary when the ash does not exceed 0·4 per cent.

The necessary quantity of hydrochloric acid, calculated from the ash, and water (50 c.c.), are placed in a flask of 500 c.c. capacity; commercial inulin (200 grams) is then introduced, and the flask is heated in boiling water for half an hour, starting from the time when the whole mass begins to soften; the acid is then neutralised with a slight excess of calcium carbonate, or with the calculated quantity of sodium hydrogen carbonate, the syrup poured into a litre of warm (commercial) absolute alcohol, a little blood-charcoal thrown in, the solution kept for 12 hours, decanted from the small quantity of syrup, and filtered. The filtrate, evaporated under reduced pressure, at a gentle heat, until it attains the consistency of a thick syrup, is then mixed with absolute alcohol (3 to 4 parts), kept for 12 hours, and the solution decanted; if a crystal of levulose is now introduced into the clear solution, and crystallisation promoted by rubbing, pure anhydrous levulose, equal in weight to one-third of the syrup, is deposited in 24 hours; after three days' time, a second crop of crystals is deposited, and further quantities can be obtained by evaporating the mother liquors at a gentle heat.

The hydrolytic decomposition of sugars in concentrated solution, by the minimum quantity of acid, which must be separately determined for each sugar, the percentage of ash being taken into consideration, will probably be found to be the most convenient and rapid method for the preparation of other glucoses. Under suitable conditions, the reversion which occurs in the hydrolysis of concentrated solutions is less than that which takes place in the evaporation of dilute solutions to the same degree of concentration. Hydrochloric acid should be employed for the purer materials, as the quantity necessary is generally so small that, as free acid, sodium chloride or calcium chloride, it does not affect the purity of the product to any appreciable extent. For substances richer in ash, sulphuric acid is used, when the product is to be purified by solution in alcohol; and hydrofluoric acid, when the product can only be crystallised from water, the acid being eliminated, after hydrolysis, by means of calcium carbonate. F. S. K.

A New Crystalline Carbohydrate. By A. v. Planta and E. Schulze (*Ber.*, **23**, 1692—1699).—The carbohydrate here described occurs in the roots of *Stachys tuberifera*, and is isolated by pressing the tubercles, extracting with water, and precipitating the liquid thus obtained with lead acetate and mercuric nitrate successively, the excess of lead and mercury being removed by sulphuretted hydrogen. The solution, after being neutralised with ammonia, is evaporated to a thin syrup and poured into alcohol, when a dark-coloured syrup is precipitated, which is dissolved in water, and phosphotungstic acid added as long as a precipitate falls. The filtrate is then treated

with baryta-water, again filtered, and carbonic anhydride passed, the precipitated barium carbonate separated, and the liquid evaporated to a small volume, and poured into absolute alcohol. After redissolving in water, and precipitating with alcohol several times, the aqueous syrup was finally poured into such a quantity of alcohol that after the addition of the syrup 9 per cent. of water was present. Part of the carbohydrate separates at once, and the filtrate on remaining for some time deposits a further quantity in hard, lustrous crystals. These may also be obtained by boiling the amorphous compound with 90 per cent. alcohol, and allowing the solution to remain.

The carbohydrate, for which the authors propose the name *stachyose*, has a slightly sweet taste, and forms a neutral solution, which rotates the plane of polarisation to the right ($[\alpha]_D = 148{\cdot}1$ in 9 per cent. solution). Its formula appears to be $C_{18}H_{32}O_{16} + 3H_2O$, the water of crystallisation being given off at 103—104°, whilst at 110—115° decomposition commences. It forms asymmetric (?) crystals ($\alpha = 88° \ 41\frac{1}{2}'$, $\beta = 90° \ 32\frac{1}{2}'$, $\gamma = 153° \ 43\frac{1}{2}'$, $a : b : c = 0{\cdot}7848 : 1 : ?$).

One of the products of inversion is galactose, the quantity of the latter formed being apparently equal to one-half that of the stachyose, and on oxidation with nitric acid it yields mucic acid.

Of the three compounds already known having the composition $C_{18}H_{32}O_{16}$, namely melitose or raffinose, gentianose, and lactosine, the last is the one with which stachyose appears to be most nearly related. H. G. C.

Products of the Saccharification of Amylaceous Substances by Acids. By G. FLOURENS (*Compt. rend.*, **110**, 1204—1206).—The constancy of the coefficient *c*, representing the rotatory power of dextrin relatively to saccharose, shows that only one dextrin is produced, as Payen supposed, and this is distinguished by its very high rotatory power, which approaches that of soluble starch. The constancy of this coefficient at different stages of saccharification shows that no maltose is formed. The results of chemical and optical examinations are in perfect agreement.

In industrial operations, the quantities of acid used are much smaller than those used in the laboratory to produce complete saccharification, and beyond a certain limit, at which 75 to 80 per cent. of the amylaceous matter has been converted into glucose, the results of the two methods of examination do not correspond. The coefficient *c* gradually diminishes, owing to decomposition and production of caramel. C. H. B.

Geometrically Isomeric Nitrogen Compounds. By C. WILLGERODT (*J. pr. Chem.* [2], **42**, 63—64).—This paper consists of further remarks on Hantzsch and Werner's paper on the subject (this vol., p. 348; compare, also, this vol., p. 576). A. G. B.

Derivatives of Propylamine. By W. E. LAUER (*Chem. Centr.*, 1890, i, 899; from *Inaug. Diss., Berlin*).—*γ-Hydroxypropylphthalimide*,

$C_6H_4<\substack{CO\\CO}>N\cdot C_3H_6\cdot OH$, prepared from bromopropylphthalimide by the action of potassium hydroxide, melts at 50—51°. *γ-Thiocyanopropylphthalimide*, $C_6H_4\!:\!C_2O_2\!:\!N\cdot C_3H_6\cdot CNS$, prepared from bromopropylphthalimide by the action of potassium thiocyanate, melts at 95°; by the action of potash it is resolved into the compound $C_{22}H_{24}KN_2S_2O_6$, potassium cyanate, potassium cyanide, and water. The white, crystalline substance melts at 136°, and has the constitution $S_2(C_3H_6\cdot NH\cdot CO\cdot C_6H_4\cdot COOH)_2$. By the action of dilute hydrochloric acid on potassium di-γ-propyldisulphide diphthalamate, the free acid is obtained.

When heated with concentrated hydrochloric acid at 200°, the disulphide is resolved into *dipropylamido-γ-disulphide*,

$$S_2(C_3H_6\cdot NH_2)_2,2HCl,$$

melting at 218—219°, and phthalic acid. The picrate of the former melts at 145—146°.

γ-Bromopropylamine hydrobromide reacts with silver sulphate, forming *γ-amidopropylsulphuric acid*, $NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot HSO_4$, melting at 221°. This has a neutral reaction, and it is, therefore, probable that the sulphuryl radical is combined with the amide radical.

From the same bromo-compound the following substances are obtained. (1.) *Bromopropylthiocarbamide*, $NH_2\cdot CS\cdot NH\cdot C_3H_6Br$, is prepared by the action of potassium thiocyanate, it melts at 127°, *trimethylenepseudothiocarbamide*, melting at 127°, obtained from the latter by separation of hydrogen bromide. (2.) *Trimethylenepseudocarbamide*, melting at 199°, is obtained by the action of potassium cyanate. (3.) μ-Mercaptopenthiazoline, $CH_2<\substack{CH_2\cdot S\\CH_2\cdot N}>C\cdot SH$, obtained by the action of carbon bisulphide, melts at 132°. It is oxidised by bromine-water to *γ-amidopropylsulphonic acid*, which melts above 300°. J. W. L.

Action of Amines on Diketopentamethylene-derivatives. By W. H. Ince (*Ber.*, **23**, 1478—1483).—The *hydrochloride* of a base of the constitution $CH_2<\substack{CHCl\cdot C\!:\!NPh\\ \vert \\ CH_2\ -C\!:\!NPh}$ is precipitated in blood-red, microscopic needles, when the sodium-derivative of 1 . 2-diketochloropentamethylene is treated with aniline in dilute acetic acid solution, and the acetate thus produced is decomposed with hydrochloric acid. It crystallises from boiling alcohol in dark-red plates, melts at 142° with decomposition, and is moderately easily soluble in alcohol, acetone, and acetic acid, but almost insoluble in water, benzene, chloroform, and dilute mineral acids; it is only slowly decomposed by alkalis, is not changed by boiling concentrated hydrochloric acid, and has the composition $C_{17}H_{15}N_2Cl,HCl + H_2O$. The free *base*, obtained by decomposing the salt with soda, is a yellow, semi-crystalline-compound, which begins to turn brown at 120°, and melts at 129° with decomposition; it gradually turns red on exposure to the air, and it yields a reddish-violet sulphate.

The *salt*, $C_{19}H_{19}N_2Cl,2C_2H_4O_2$, separates in yellowish-red crystals,

when the sodium-derivative of 1 . 2-diketochloropentamethylene is treated with paratoluidine in acetic acid solution. It melts at about 160° with decomposition, and is readily soluble in alcohol, ether, and chloroform, but only moderately easily in acetic acid. The *hydrochloride*, $C_{19}H_{19}N_2Cl,HCl$, separates from alcohol, in which it is readily soluble, in reddish-violet crystals, and decomposes at about 130°. The free *base* crystallises from ether in long, yellowish needles, melting at 135° with decomposition.

A *base* of the composition, $C_{12}H_{12}ClNO$, is precipitated as an oil when the sodium-derivative of 1 . 2-diketochloropentamethylene is added to a concentrated, neutral solution of methylaniline hydrochloride. It separates from alcohol in yellow crystals which melt at 126—127°; the *hydrochloride* is readily soluble, but the *platinochloride* can be precipitated directly. A crystalline *base*, melting at 153°, can be obtained with methylamine in like manner, but in the case of ethylamine and dimethylamine no definite product could be isolated.

The *acetate* of a base separates in microscopic crystals when 1 . 3-diketochloropentamethylene is treated with aniline in acetic acid solution. It melts at 190° with decomposition, and is soluble in acetone and dilute acids, but insoluble in ether; it is slowly decomposed by soda, and quickly by concentrated hydrochloric acid.

The crystalline *salt*, $C_{19}H_{18}Cl_2N_2,C_2H_4O_2$, obtained from 1 . 3-diketochloropentamethylene and paratoluidine in like manner, melts at 150° with decomposition; the free base is a yellow powder almost insoluble in ether. F. S. K.

Breaking the Pentamethylene Ring. By A. HANTZSCH (*Ber.*, **23**, 1483—1489).—Ince's investigations (preceding abstract) have shown that the derivatives of the diketopentamethylenes behave like diketones with amines and with amido-compounds; it is nevertheless probable that under the influence of water or alkalis these pentamethylene-compounds are converted into open-chain-derivatives, which are reconverted into pentamethylene-derivatives when they separate from their solutions. The sodium-derivative of 1 . 2-diketochloropentamethylene, for example, which is an intensely yellow, solid compound, gives colourless, neutral solutions; this phenomena may be explained by assuming that the solid has the constitution $CH_2<\begin{matrix}CClNa\\CH_2\cdot CO\end{matrix}>CO$ or $CH_2<\begin{matrix}CCl:C(ONa)\\CH_2\cdot\overset{|}{C}O\end{matrix}$, but that in solution it exists as the true sodium salt of the aldehyde acid, $COOH\cdot CHCl\cdot CH_2\cdot CH_2\cdot CHO$. Some observations which were made by Ostwald, whilst engaged in measuring the electrical conductivity of these compounds, lend probability to this view.

Tri- and tetra-chlorodiketopentamethylenehydroxycarboxylic acids both behave like true dicarboxylic acids, a fact which can be explained only by assuming that in aqueous solution and in their salts they have the constitution $COOH\cdot CO\cdot CHCl\cdot C(OH)(COOH)\cdot CHCl_2$ and $COOH\cdot CO\cdot CCl_2\cdot C(OH)(COOH)\cdot CHCl_2$ respectively.

1 . 3-Diketodichloropentamethylene, under the influence of alkalis, is probably converted into the salt of the ketone acid

$$COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CHCl_2,$$

just as dichlorodiketohydrindene is converted into salts of dichloroacetophenonecarboxylic acid (compare Zincke, Abstr., 1888, 1192).

F. S. K.

Formaldehyde. By K. Kraut, W. Eschweiler, and G. Grossmann (*Annalen*, **258**, 95—110).—Crude formaldehyde, prepared from sodium hydroxymethylsulphonate, contains about 0·04 to 0·07 per cent. of formic acid and considerable quantities of methyl alcohol, but it can be obtained free from these impurities by first shaking with calcium carbonate and then fractionating; the methyl alcohol accumulates in the lower boiling (80—90°) fractions, whilst the highest boiling (98·5—99°) fractions consist of pure aqueous formaldehyde. This solution can be concentrated by distillation over calcium carbonate until it contains 52·4 per cent. of formaldehyde, but a stronger solution cannot be obtained owing to polymerisation.

The authors' experiments seem to show that oxymethylene dissolves unchanged in water, and then gradually becomes converted into formaldehyde, this change taking place more quickly in warm dilute than in cold concentrated solutions. Determinations of the molecular weight of formaldehyde in aqueous solution gave results which show, as did those obtained by Tollens (Abstr., 1888, 809), that a freshly prepared solution of formaldehyde, diluted with cold water, contains a substance, the molecular weight of which is higher than that of the aldehyde.

Sodium hydroxymethylenesulphonate (*formaldehyde sodium hydrogen sulphite*), $CH_2O,NaHSO_3 + H_2O$, is deposited in well-defined, transparent plates, $a : b : c = 1{\cdot}7750 : 1 : 0{\cdot}6251$, $\beta = 68° 1'$, when an aqueous solution of formaldehyde, or when solid oxymethylene is treated with a concentrated solution of sodium hydrogen sulphite, and the salt precipitated with alcohol. It loses 1 mol. H_2O over sulphuric acid, is decomposed by boiling water, and is readily soluble in water and methyl alcohol, but only very sparingly in ethyl alcohol. The *potassium* salt, obtained in like manner, forms large anhydrous plates, and also monosymmetric crystals,

$$a : b : c = 2{\cdot}8400 : 1 : 1{\cdot}0368,\ \beta = 81°\ 47\tfrac{2}{3}',$$

which rapidly effloresce.

Methylenedipiperidine, $C_{11}H_{22}N_2$, is formed when piperidine is added to an aqueous solution of sodium hydroxymethylsulphonate; it boils at 234—235·5°, and is decomposed by hydrochloric acid. Methylenedibenzamide (hipparaffin), $C_{15}H_{14}N_2O_2$, melts at 220°. F. S. K.

Action of Hydrogen Sulphide on Aldehydes. By E. Baumann (*Ber.*, **23**, 1869—1876; compare this vol., p. 477).—A neutral solution of formaldehyde is well cooled and saturated with hydrogen sulphide; a colourless liquid is obtained, from which a voluminous crystalline precipitate is deposited on the addition of an equal bulk of hydrochloric acid (5 per cent.); the substance is washed with water,

and treated with a saturated alcoholic solution of iodine, a resinous mass is formed, from which *trimethylene tetrasulphide*, $CH_2<\substack{S\cdot CH_2\cdot S\\S\cdot S\cdot CH_2}>$ is extracted by repeatedly boiling with alcohol; it crystallises in colourless needles melting at 83—84°. This compound is derived from dithiomethylenemercaptan, $SH\cdot CH_2\cdot S\cdot CH_2\cdot S\cdot CH_2\cdot SH$. The resinous mass remaining after the removal of the tetrasulphide is insoluble in all media; it may be purified by treatment with alcohol, and melts at 135—137°. *Dimethyldimethylenetrisulphone*,

$$SO_2(CH_2\cdot SO_2Me)_2,$$

is prepared by treating formaldehyde with hydrogen sulphide and extracting the solution with ether; the residue, obtained after evaporating the ether, is dissolved in dilute aqueous soda and treated with excess of methyl iodide; a mixture of thioethers is thus formed, which cannot be separated without their undergoing decomposition; the oily liquid is treated with an acid solution of potassium permanganate, and, on evaporating the solution, the trisulphone crystallises in long, thin prisms melting at 184—185°; it is very sparingly soluble except in hot water, and forms uncrystallisable salts with the alkalis. This compound is formed from thiodimethylenemercaptan, $S(CH_2\cdot SH)_2$. *Tetrabromodimethyldimethylenetrisulphone*,

$$SO_2(CBr_2\cdot SO_2Me)_2,$$

is prepared by the action of bromine-water on an aqueous solution of the sulphone; it crystallises in small scales melting at 190° with decomposition. *Diethyldimethylenetrisulphone*, $SO_2(CH_2\cdot SO_2Et)_2$, obtained from ethyl bromide in a manner similar to the dimethyl compound, crystallises in colourless scales; it melts at 149°, and yields a *tetrabromide*.

On further concentrating the mother-liquors remaining after the separation of the dimethyldimethylenetrisulphone, tabular crystals of dimethylmethylenedisulphone, $CH_2(SO_2Me)_2$, are deposited, melting at 141°; diethylmethylenedisulphone, $CH_2(SO_2Et)_2$, is obtained in the same way from the mother-liquors of diethyldimethylenetrisulphone. Both these compounds are already known; they are evidently derived from methylenemercaptan, $CH_2(SH)_2$, which has not yet been obtained in the pure state. J. B. T.

Chloralimide and its Isomeride. By BÉHAL and CHOAY (*Compt. rend.*, **110**, 1270—1273).—500 grams of chloral ammonia is mixed with 200 grams of anhydrous chloral and distilled on a water-bath until 100 grams of chloroform have been collected. From this point distillation is continued in a vacuum until nothing more passes over. The residue is exhausted with cold alcohol of 95°; chloralimide remains undissolved (this vol., p. 230) and isochloralimide passes into solution. Isochloralimide is precipitated by the addition of dilute alcohol and purified by repeated crystallisation from boiling alcohol of 90°. It is insoluble in water, melts at 103—104°, is decomposed by mineral acids with liberation of chloral and formation of the corresponding ammonium salt, and is even decomposed by platinic

chloride with formation of ammonium platinochloride. When heated with alkalis, it evolves an odour of carbylamines, ammonia is liberated, and a formate and chloroform are produced.

Isochloralimide and chloralimide have the same composition, and determinations of the molecular weight by Raoult's method, in solution in benzene, gave a number corresponding in both cases to the molecular weight 439·5, which agrees with the triple formulæ previously adopted (*loc. cit.*).

If isochloralimide is heated with methyl chloride in a sealed tube at 100°, it is converted into chloralimide, and if the latter is dissolved in chloroform and mixed with 3 mols. of bromine, it is converted into isochloralimide. Acid chlorides give the same compounds with both isomerides, and these products, which are very stable, will be described subsequently.

The authors ascribe to the two isomerides the following constitution:—

$$NH{<}{\begin{matrix}CH(CCl_3)\cdot NH\\CH(CCl_3)\cdot NH\end{matrix}}{>}CH\cdot CCl_3. \qquad NH_2{<}{\begin{matrix}C(CCl_3)\cdot NH_2\\C(CCl_3)\colon NH_2\end{matrix}}{>}C\cdot CCl_3.$$

Chloralimide. Isochloralimide.

The presence of the amido-group in isochloralimide is indicated by its greater solubility, and by the production of chloroform and a carbylamine when treated with an alkali.

The ready migration of the hydrogen which is combined with the nitrogen throws considerable light on the splitting up of diazoamido-derivatives.

Adopting Bonveault's nomenclature, chloralimide is tertrichlormethyl triazidine (1 : 3 : 5) and the authors propose to denote the analogous compounds containing the amido- group by the name triazidiniums. Isochloralimide will then be tertrichloromethyltriazidinium (1 : 3 : 5). C. H. B.

The so-called Cyanacetone. By A. HANTZSCH (*Ber.*, **23**, 1472—1474).—An energetic reaction sets in when chloracetone (1 mol.) is poured into an aqueous solution of potassium cyanide; the product, which is not cyanacetone, but a complicated condensation-product, crystallises from alcohol, in which it is readily soluble, in small needles, melts at 176°, and has the composition $C_{10}H_{13}N_3O_2$. It is tasteless and odourless, and only moderately easily soluble in hot water and ether. It is doubtless identical with the "cyanacetone" described by Glutz (*J. pr. Chem.* [1], **39**), but its chemical behaviour indicates a high molecular weight; it cannot be readily decomposed into acetone or acetic acid and carbonic anhydride, and when treated with acids or alkalis it yields a complex compound melting at 65°.

When potassium cyanide is treated with chloracetone in alcoholic solution, a dark oil, boiling above 120°, is obtained in very small quantity (compare Matthews and Hodkinson, Abstr., 1883, 311), together with considerable quantities of non-volatile substances.

F. S. K.

Cyanacetone. By A. HANTZSCH (*Ber.*, **23**, 1816; compare preceding abstract).—An apology for overlooking the fact that Holtzwart (Abstr., 1889, 683) had already prepared cyanacetone. The constitution of the compound formed by the action of potassium cyanide on chloracetone is probably best represented by the formula CN·CH·Ac·C·OH·Me·CH_2·CN. J. B. T.

Chloro-substitution-products of Ethyl Chloroformate.—By H. MÜLLER (*Annalen*, **258**, 50—66; compare Hentschel, Abstr., 1887, 1099; 1888, 248 and 249).—Various chloro-substitution-products are formed, together with small quantities of hexachlorethane, when chlorine is passed into boiling ethyl chloroformate which is exposed to direct sunlight; the liquid is fractionated after the gas has been passed for a short time in order to isolate the compounds of lower boiling point, the lowest and the highest fractions are then chlorinated and fractionated again. In this way the compounds described below were isolated.

α-Chlorethyl chloroformate, ClCO·O·C_2H_4Cl, is a colourless liquid of sp. gr. 1·325 at 15°, and boils at 118—119°; when treated with a small quantity of aluminium chloride, it is decomposed into ethylidene chloride and chlorethylene, and when warmed with water, it yields carbonic anhydride, hydrochloric acid, and acetaldehyde; hot alcohol converts it into α-chlorethyl ethyl carbonate,

OEt·CO·O·CHClMe,

which on further boiling is completely decomposed into hydrogen chloride, ethyl chloride, and acetaldehyde.

The fraction boiling at 153·5—154·5° consists of a compound of the composition $C_6H_7Cl_5O_4$, which seems to be formed by the combination of an equal number of molecules of α-chlorethyl chloroformate and dichlorethyl chloroformate. Determinations of the vapour density of this compound showed that it decomposes into its constituents at its boiling point; it cannot, however, be separated into its constituents by fractional distillation, nor can it be formed by mixing them in the right proportion. When treated with aluminium chloride, it is decomposed into carbonic anhydride, ethylidene dichloride, and chlorethylene dichloride.

αβ-Dichlorethyl chloroformate, ClCO·O·$C_2H_3Cl_2$, is a colourless liquid of sp. gr. 1·510 at 15°, and boils at 159—160°; aluminium chloride decomposes it into carbonic anhydride and chlorethylene dichloride, and alcohol converts it into ethyl αβ-dichlorethyl carbonate, a colourless oil boiling at 195—196°.

Trichlorethyl chloroformate, ClCO·O·CCl_2·CH_2Cl, is an oil of sp. gr. 1·584 at 15°, and boils at 169—170°; it is decomposed by aluminium chloride into carbonic anhydride, hydrochloric acid, asymmetrical tetrachlorethane (b. p. 134—136°), and a liquid—probably trichlorethylene—which boils at 85—90°.

Tetrachlorethyl chloroformate, ClCO·O·CCl_2·$CHCl_2$, is an oil of sp. gr. 1·660 at 15°, and boils at 176—177°; it is decomposed by aluminium chloride into carbonic anhydride, hydrogen chloride, and tetrachlorethylene.

Perchlorethyl chloroformate, $ClCO \cdot O \cdot C_2Cl_5$, is an oil of sp. gr. 1·702 at 15°, and boils at 140—141° (110 mm.); under the ordinary pressure it boils at 184—185° with slight decomposition into carbonyl chloride, carbonic anhydride, hexachlorethane, and trichloracetic chloride (compare Cloez, *Annalen*, **60**, 259). It is decomposed by aluminium chloride into carbonic anhydride and hexachlorethane, and when boiled with water it also yields hexachlorethane and carbonic anhydride, only small quantities of trichloracetic acid being formed. When treated with ammonia, the principal product is either chloroform or trichloracetamide, according to the conditions of the experiment, small quantities of hexachlorethane being also produced.

All the chlorinated ethyl chloroformates produce sores on the skin and their vapour is exceedingly irritating. F. S. K.

Action of Bromine on Trimethylacetic Acid. By S. REFORMATZKY (*Ber.*, **23**, 1594—1598).—Trimethylacetic acid was prepared according to the method of Friedel and Silva from pinacone hydrate by gently boiling it in a reflux apparatus with dilute sulphuric acid, and oxidising the pinacoline formed by adding chromic acid mixture and again gently boiling the solution. Water was then added, and the liquid distilled until sulphuric acid began to vaporise. The distillate was freed from unaltered pinacoline by extraction with ether, evaporated, treated with dilute sulphuric acid, and extracted with ether. After evaporating the ether from the extract, a residue of trimethylpyruvic, acetic, and trimethylacetic acids was obtained, and the trimethylacetic acid was separated by fractionation; it boiled at 155—163°. By treating it with bromine and phosphorus, and pouring the product into alcohol, ethyl trimethylacetate and small quantities of bromine-derivatives of hydrocarbons were obtained, but no bromotrimethyl acetate. Trimethylacetic chloride was then made by the action of phosphorus trichloride on the acid; it boiled at 100—110°. When heated with bromine in a sealed tube at 100° and finally to 135°, it yielded a mixture of bromine-derivatives of hydrocarbons, but no bromotrimethylacetic derivative. It appears that in general, acids which contain no hydrogen in the α-position are incapable of exchanging a hydrogen atom for bromine. C. F. B.

Action of Alcohols on Ethyl Acetoacetate. By T. PETERS (*Annalen*, **257**, 353—358).—When ethyl acetoacetate (30 grams) is mixed with methyl alcohol (150 grams) in which a small quantity of sodium (0·5 gram) has been dissolved, and the mixture is kept at the ordinary temperature, the ethyl acetoacetate is gradually and completely converted into the methyl salt; isoamyl alcohol, under the same conditions, converts the ethyl into the isoamyl salt. The same changes take place, but much more quickly (in 16 to 20 hours), when ethyl acetoacetate is boiled with either of the above-named alcohols, and isobutyl alcohol, under the same conditions, transforms the ethyl into the isobutyl salt. Isobutyl and isoamyl alcohol convert ethyl acetoacetate into the isobutyl and isoamyl salts respectively, even in absence of sodium, but prolonged boiling is required, and a large excess of the alcohol must be employed; methyl alcohol has no action

on ethyl acetoacetate and ethyl ethylacetoacetate in absence of sodium. Ethyl isobutylacetoacetate boils at 198—202°, isobutyl ethylacetoacetate at 211—215°, isoamyl acetoacetate at 217—219°, and isoamyl ethylacetoacetate at 226—230°. F. S. K.

Behaviour of Ethereal Salts of Alkyl-substituted Acetoacetic Acid with Ammonia. By T. PETERS (*Annalen*, **257**, 339—353).—Two classes of compounds are formed by the action of ammonia on ethereal salts of the alkyl-derivatives of acetoacetic acid, namely, the ethereal salt of an α-alkyl-β-amidocrotonic acid and the amide of an alkylacetoacetic acid; the former is alone produced when anhydrous ammonia is employed.

With ammonia, methyl ethylacetoacetate yields methyl ethylamidocrotonate (m. p. 35—36°) and ethylacetoacetamide (m. p. 96°), but not methylacetoacetamide, as stated by Brandes.

Methylacetoacetamide, $COMe{\cdot}CHMe{\cdot}CO{\cdot}NH_2$, prepared from ethyl methylacetoacetate, crystallises from ether in colourless needles melting at 73°. Ethyl α-methyl-β-amidocrotonate melts at 53° and is readily soluble in alcohol, ether, and benzene.

Isobutylacetoacetamide melts at 88°; *ethyl α-isobutyl-β-amidocrotonate* at 41—42°.

Isoamylacetoacetamide, $COMe{\cdot}CH(C_5H_{11}){\cdot}CO{\cdot}NH_2$, melts at 129°; *ethyl α-isoamyl-β-amidocrotonate*, $NH_2{\cdot}CMe{:}C(C_5H_{11}){\cdot}COOEt$, at 50°.

Ethyl diethylacetoacetate is not acted on either by anhydrous or aqueous ammonia. F. S. K.

Decomposition-products of the Sodium Salts of the Chlorolactic Acids. By E. REISSE (*Annalen*, **257**, 331—338).—When an aqueous solution of sodium trichlorolactate is heated at about 75—80°, it is decomposed into sodium chloride and dichloraldehyde with evolution of carbonic anhydride; the presence of the dichloraldehyde was proved by oxidising a portion of the distilled solution with nitric acid and isolating the dichloracetic acid thus produced, as well as by various other tests.

An aqueous solution of sodium dichlorolactate is slowly decomposed at 95° into chloraldehyde and sodium chloride, with evolution of carbonic anhydride; a solution of the chlorolactate, at the same temperature, undergoes decomposition into aldehyde, carbonic anhydride, and sodium chloride, small quantities of glyceric acid being also formed. F. S. K.

Brominated Pyrotartaric Acids. By C. A. BISCHOFF (*Ber.*, **23** 1924—1929).—The author has previously shown, in conjunction with Guthzeit (Abstr., 1881, 579), and with Emmert (Abstr., 1882, 1191), that the products of bromination of propenyltricarboxylic acid are a monobromopyrotartaric acid melting at 202—204°, a brominated crotonic acid melting at 107—109°, apparently identical with Michael and Norton's α-bromocrotonic acid, and a dibromopyrotartaric acid melting at 127—128°. Two isomerides of the latter acid are known, melting at 204° and 170° respectively, both of which can be converted into bromomethacrylic acid, $CHBr{:}CMe{\cdot}COOH$. The first-

mentioned dibromopyrotartaric acid, on the other hand, is converted by alkalis into α-bromocrotonic acid, which has, according to Wislicenus, the constitution $\begin{array}{c}H\cdot C\cdot CH_3\\ \| \\ Br\cdot C\cdot COOH\end{array}$. The acid from which it is obtained must therefore contain both bromine-atoms combined with the same carbon-atom, $\begin{array}{c}CH_3\cdot CH\cdot COOH\\ | \\ Br_2C\cdot COOH\end{array}$.

In addition to the above monobromopyrotartaric acid melting at 202—204°, two isomeric acids are known which melt at 137° and 148° respectively. The first of these gives paraconic acid on boiling with water, and itaconic acid on treatment with soda, and has therefore probably the constitution $\begin{array}{c}CH_2\cdot Br\\ | \\ H\cdot C\cdot COOH\\ | \\ H\cdot C\cdot COOH\\ | \\ H\end{array}$, whilst the second when treated with soda yields methacrylic acid, which leads to the constitution $\begin{array}{c}CH_3\\ | \\ Br\cdot C\cdot COOH\\ | \\ H\cdot C\cdot COOH\\ | \\ H\end{array}$. The acid melting at 202—204° was obtained in larger quantity by adding bromine to an aqueous solution of propenyltricarboxylic acid, and concentrating the solution, carbonic anhydride being given off. It was thus obtained in hard prisms melting at 203·5°. Only one structural formula is possible for this acid, which can, however, exist in two geometrically isomeric forms, namely, $\begin{array}{c}CH_3\\ | \\ H\cdot C\cdot COOH\\ | \\ Br\cdot C\cdot COOH\\ | \\ H\end{array}$ and $\begin{array}{c}CH_3\\ | \\ H\cdot C\cdot COOH\\ | \\ Br\cdot C\cdot H\\ | \\ COOH\end{array}$. On heating it at 210° in an oil-bath, hydrogen bromide and water are given off, and citraconic anhydride distils over. The acid may be termed "parasymmetrical bromomethylsuccinic acid." H. G. C.

Determination of the Structure of Aliphatic Acids, and the so-called "Dynamical Isomerism." By K. AUWERS and L. L. JACKSON (*Ber.*, **23**, 1599—1617).—This paper is the first of a series which is to describe a study of the action of bromine on aliphatic acids, and of the electric conductivity of the latter, and to show how these data may be used to determine the constitution of such acids. In the first or introductory portion of the paper, it is shown that the acid obtained by treating ethyl methylsodiomalonate with ethyl-α-bromisobutyrate and saponifying the product with sulphuric acid is not trimethylsuccinic, but symmetrical αα-dimethylglutaric acid. The isomeric derivatives of succinic acid lately discovered by Bischoff (this vol., pp. 741—744) are then discussed, and it is stated that there is no need to resort to "dynamical isomerism" to explain the existence of these, as many of them are probably derivatives of glutaric acid, formed by a molecular transformation similar to that mentioned

above, and are thus *chemical* isomerides of the succinic acid derivatives.

αα-Dimethylglutaric acid, COOH·CHMe·CH_2·CHMe·COOH, was obtained by dissolving 4·6 grams of sodium in 80 c.c. of absolute alcohol, cooling the solution, adding 34·8 grams of ethyl methylmalonate, and warming on the water-bath, cooling, adding 39 grams of bromisobutyric acid, and again warming. The product was isolated and purified, and the portion boiling at 250—290° (38 per cent. of the theoretical yield) saponified by boiling with dilute sulphuric acid. On cooling the solution, αα-dimethylglutaric acid was obtained in needles melting at 105—106°, soluble in all ordinary solvents except light petroleum, and not volatile with steam. Its coefficient of electrical conductivity (K) is 0·00524. When boiled for a few minutes, it forms an *anhydride*, which can be isolated by treating the liquid with soda, and crystallises from light petroleum in thin, rectangular prisms melting at 92—93°. By treating the acid with red phosphorus and bromine, *αα-dibromo-αα-dimethylglutaric anhydride*, $CH_2<\begin{matrix}CMeBr\cdot CO\\CMeBr\cdot CO\end{matrix}>O$, is obtained. It is an unstable substance, crystallising from light petroleum in oblique prisms which melt at 92—93°, and sublime without decomposition. When it is treated with cold aqueous soda, and the solution neutralised with sulphuric acid, ether extracts a substance which crystallises in colourless, hexagonal plates melting at 95—96°, and is probably *dihydroxydimethyglutaric acid*, CH_2[CMe(OH)·COOH]$_2$.

Glutaric acid was then prepared by decomposing its silver salt with hydrogen sulphide, and was treated with excess of bromine in the presence of phosphorus. No brominated acid was obtained in this way, but an unstable substance which decomposed when heated, and was doubtless glutaric bromide. It was poured into excess of alcohol, and the solution evaporated; the residue consisted of a mixture of ethyl dibromo- and monobromo-glutarates in the proportion of about three parts of the former to one of the latter. C. F. B.

Trimethylsuccinic Acid and Dimethylglutaric Acid. By C. A. Bischoff (*Ber.*, **23**, 1464—1468).—A symmetrical dimethylglutaric acid melting at 100—101° can be obtained by treating ethyl sodiomethylmalonate (2 mols.) with methylene iodide, hydrolysing the ethereal salt thus produced, and heating the acid until the evolution of carbonic anhydride is at an end. The electrical conductivity of this acid is the same as that of the trimethylsuccinic acid obtained from ethyl methylmalonate and ethyl bromisobntyrate, and that of Zelinsky's symmetrical dimethylglutaric acid (m. p. 102—103°); the three acids have also the same crystalline form and the same solubility, so that a further comparison of the derivatives of the three compounds will probably prove their identity. The author has succeeded in synthesising mesaconic and citraconic acids from ethyl malonate. F. S. K.

γ-Ketone-Acids. By C. Paal and T. Hoffmann (*Ber.*, **23**, 1495—1505).—*Ethyl isoamylmalonate*, C_5H_{11}·CH(COOEt)$_2$, prepared

by treating ethyl sodiomalonate with isoamyl bromide in alcoholic solution, is a colourless, mobile oil, with an agreeable fruity odour; it boils at 240—242°, and is insoluble in water. The free *acid*, $C_8H_{14}O_4$, is obtained by boiling the ethereal salt for several hours with concentrated potash; it crystallises from a mixture of benzene and light petroleum in colourless needles, melts at 93° with evolution of carbonic anhydride, and is readily soluble in water, alcohol, ether, ethyl acetate, and hot benzene, but only sparingly in light petroleum. The *ammonium* salt crystallises in needles or prisms. The *sodium* salt separates from dilute alcohol in ill-defined crystals. The *calcium* salt, $C_8H_{12}O_4Ca$, and the *barium* salt seem to be amorphous, and are insoluble in water. The *silver* salt, $C_8H_{12}O_4Ag_2$, is amorphous and moderately stable. In aqueous solutions of the ammonium salt, ferric chloride produces a red, and copper sulphate a bluish-green precipitate. The *amide*, $C_5H_{11}·CH(CO·NH_2)_2$, prepared by heating the ethereal salt with concentrated alcoholic ammonia at 150°, crystallises from alcohol in colourless needles, melts at 210°, and is readily soluble in hot alcohol but only sparingly in benzene, and insoluble in ether and light petroleum.

Isoamylacetic acid, $C_7H_{14}O_2$, is obtained by heating isoamylmalonic acid; it is a colourless, disagreeably smelling oil of sp. gr. 0·912243 at 19°, compared with water at the same temperature; it boils at 208—210°, and is very sparingly soluble in water. The *ethyl* salt, $C_9H_{18}O_2$, prepared by passing hydrogen chloride into an alcoholic solution of the acid, is a colourless oil of pleasant odour, boiling at 177°. The *calcium* salt, $C_{14}H_{26}O_4Ca$, is crystalline and only sparingly soluble in hot water.

Ethyl phenacylisoamylmalonate, $COPh·CH_2·C(C_5H_{11})(COOEt)_2$, can be prepared by gradually adding phenacyl bromide to a well-cooled ethereal solution of ethyl sodioisoamylmalonate and then warming the mixture for a short time, but it is obtained in a less impure condition by passing hydrogen chloride into an alcoholic solution of phenacylisoamylmalonic acid; the crude product is a thick, colourless oil. The free *acid*, $C_{16}H_{20}O_5$, prepared by hydrolising the crude ethereal salt with alcoholic potash, crystallises from dilute alcohol, or acetic acid, in long, colourless needles, melts at 160°, and is readily soluble in alcohol, ether, ethyl acetate, and glacial acetic acid, but almost insoluble in benzene and light petroleum; when crystallised from water or from solvents containing water, it invariably contains small quantities of water, from which it cannot easily be freed. The *potassium* salt crystallises in plates and is readily soluble in water and hot alcohol. The *ammonium* salt, $C_{16}H_{19}O_5·NH_4$, crystallises in needles, melts at 165°, and is moderately easily soluble in cold water. When the acid is heated with phosphoric chloride and phosphorus oxychloride, it is converted into the chloride, which is so unstable that it cannot be obtained in a pure condition. Both the acid and the ethyl salt combine with hydroxylamine, yielding oximes.

Attempts to convert phenacylisoamylmalonic acid and phenacylisoamylacetic acid (see below) into 1.3-phenylisoamylthiophen, by heating with phosphorus trisulphide, were unsuccessful.

Octylbenzene, $CHMe_2·[CH_2]_4·CH_2Ph$, is obtained when phenacyl-

isoamylmalonic acid is distilled over zinc-dust and the product fractionated over sodium; it is a colourless, mobile oil, boiling at about 245—255°, and possessing an aromatic odour.

β-Phenyl-β-hydroxy-α-isoamylethylmalonic acid,

$$OH{\cdot}CHPh{\cdot}CH_2{\cdot}C(COOH)_2{\cdot}C_5H_{11},$$

can be prepared by reducing a dilute alcoholic solution of phenacylisoamylmalonic acid with sodium amalgam, the solution being kept slightly acid by the frequent addition of dilute sulphuric acid. It is a gum-like substance, readily soluble in ether, alcohol, and glacial acetic acid, but almost insoluble in water; when heated, it is converted into *γ-phenyl-α-isoamylbutyrolactone*, $CHPh<\begin{smallmatrix}-CH_2\\O{\cdot}CO\end{smallmatrix}>CH{\cdot}C_5H_{11}$, with evolution of water and carbonic anhydride.

Phenacylisoamylacetic acid (*β-benzoyl-α-isoamylpropionic acid*), $COPh{\cdot}CH_2{\cdot}CH(C_5H_{11}){\cdot}COOH$, prepared by heating the preceding compound above its melting point, crystallises from dilute alcohol or light petroleum in colourless plates, melts at 103°, and is readily soluble in alcohol, ether, and benzene, but only sparingly in light petroleum, and insoluble in water. The *ethyl* salt is a colourless oil boiling at 260°. When the acid is boiled for some time, it is converted into *γ-phenyl-α-isoamylbutenyllactone* (b. p. about 310—320°), which, however, cannot be obtained in a pure condition. F. S. K.

Synthesis of Mesaconic and Citraconic Acids from Ethyl Propenyltricarboxylate. By C. A. Bischoff (*Ber.*, **23**, 1930—1937).—In previous papers by the author and by Guthzeit, it has been shown that almost all alkyl-substituted ethyl malonates are readily acted on by chlorine at 100°. Ethyl acetylenetetracarboxylate forms an exception, as it is only attacked at 200°, and then passes into the ethyl salt of a tribasic acid. By the action of chlorine on ethyl propenyltricarboxylate on the water-bath, no chloro-derivative corresponding with ethyl chloromalonate can be obtained; if, however, the ethyl salt is heated to 180—200°, substitution takes place in the normal manner, *ethyl chloropropenyltricarboxylate*, $\begin{matrix}Cl{\cdot}C(COOEt)_2\\|\\Me{\cdot}CH{\cdot}COOEt\end{matrix}$, being obtained as a yellow oil with a pungent odour, boiling at 287—288° under 770 mm. pressure. By the action of hydrochloric acid, it yields mesaconic acid and carboxymesaconic acid,

$$COOH{\cdot}CMe{:}C(COOH)_2,$$

melting at 168°; the latter readily loses carbonic anhydride with formation of mesaconic acid. A third product was also obtained, which appears to be impure citraconic acid.

Ethyl butenyltricarboxylate, when treated with chlorine in an analogous manner, yields a monochloro-derivative of a similar character, boiling at 292°. On hydrolysis, it is converted into ethylmaleic acid, $\begin{matrix}H{\cdot}C{\cdot}COOH\\||\\Et{\cdot}C{\cdot}COOH\end{matrix}$, melting at 90—92°, which is quite stable, whereas the isomeric pyrocinchonic acid exists only as an anhydride.

H. G. C.

Citraconanil and Pyranilpyroïnlactone. By A. REISSERT (*Ber.*, **23**, 1620—1621).—A reply to the paper of Anschütz (compare Abstr., this vol., p. 774) regarding the identity of these compounds. The author points out that the production of anilidopyrotartaric acid by reduction affords no proof of the constitution of either citraconanil or pyranilpyroïnlactone, as its formation is equally well explained by either of the formulæ in dispute. On oxidation, citraconanil yields oxanilic acid, whilst anilosuccinic acid is obtained from pyranilpyroïnlactone. These facts, together with the different physical properties of the two compounds, confirm the author in his opinion that they are distinct substances. J. B. T.

Condensation of Ketone Acids with Dicarboxylic Acids. By R. FITTIG and G. PARKER (*Ber.*, **23**, 1535—1536).—The compound of the composition $C_6H_6O_3$, which was obtained by the condensation of pyruvic acid with sodium succinate (Abstr., 1889, 1146), is not an acid, but the anhydride of pyrocinchonic acid. F. S. K.

Combination of Malic Acid with normal Potassium and Sodium Tungstates. By D. GERNEZ (*Compt. rend.*, **110**, 1365—1368; compare this vol., 744).—The solutions examined contained 1·1166 grams of malic acid, various proportions of the tungstate, and water sufficient to make the volume of the solution up to 24 c.c. at 15°; the rotation of the malic acid solution alone was 15′ at 17° in a tube 201·5 mm. long.

The addition of equal weights of the alkaline tungstate increases the rotatory power by equal increments until a maximum is reached, when equal equivalents of the acid and the tungstate are present. Further addition of tungstate results in a gradual reduction of the rotatory power, which changes its sign and attains a second maximum when two equivalents of the salt are present to one of malic acid. Beyond this point the rotatory power again diminishes, again changes in sign, and reaches another maximum when five equivalents of the salt are present to two equivalents of malic acid. If further quantities of tungstate are added, the rotatory power again passes from left to right, and a gradual increase in the rotatory power indicates the formation of a combination of one equivalent of the acid and eight equivalents of the tungstate. C. H. B.

Distillation Products of Citrates. By C. A. BISCHOFF and A. HAUSDÖRFER (*Ber.*, **23**, 1915—1918).—When a mixture of citric acid, quicklime, and iron filings is distilled in an iron retort, a distillate is obtained which consists of an aqueous and an oily portion. The latter on repeated fractionation gave products boiling at 58—60°, 90°, 120°, and 210°. The first consisted of acetone, and the authors regarded the second as metacetone until the publication of E. Fischer and Laycock's researches showed this to be a mixture (Abstr., 1889, 487). None of the other fractions consists of hydrocarbons.

The distillation was next repeated on a larger scale, 6·5 kilos. of sodium citrate being employed. The fractions of the oil boiling at 45—80° and 80—115° were washed with soda solution and dried over

potassium carbonate. The portions boiling above 90°, collected in fractions of 10° range, were treated with phenylhydrazine, heated on the water-bath, and finally dried on the oil-bath at 180°. The residue, on fractionation in a vacuum, yielded propaldehydephenylhydrazone as a yellow oil, which was converted into scatole on heating with zinc chloride.

The higher boiling portions likewise reduce silver solution, but are stable towards oxidising agents, and are therefore probably not aldehydes. The fractions analysed show the characteristic reactions of substituted furfurans, and the numbers obtained on analysis in two cases agree with those required for triallylfurfuran and dipropylfurfuran.

H. G. C.

Action of Ethyl α-Bromisobutyrate on Ethyl Propylmalonate and Isopropylmalonate. By C. A. Bischoff and A. Tigerstedt (*Ber.*, **23**, 1937—1941).—When ethyl propylmalonate is mixed with an alcoholic solution of sodium ethoxide, and ethyl α-bromisobutyrate added, the normal reaction takes place, the ethyl salt of a tricarboxylic acid being formed. This has the composition $C_{16}H_{28}O_6$, and forms a slightly yellowish oil, which boils at 300—301°. It cannot be obtained from ethyl isobutenyltricarboxylate by the action of sodium ethoxide and propyl iodide.

On hydrolysis, the ethyl salt yields the corresponding *propylisobutenyltricarboxylic acid*, $C_{10}H_{16}O_6$, which crystallises in colourless nodules, readily soluble in water and ether. At 167—168°, it melts, giving off carbonic anhydride and forming a dicarboxylic acid. The latter was found to be a mixture of two geometrically isomeric acids, melting at 51—53° and 101—102° respectively. They readily pass one into the other, and are probably *symmetrical methylpropylglutaric acids*, $COOH{\cdot}CHPr^{\alpha}{\cdot}CH_2{\cdot}CHMe{\cdot}COOH$.

When ethyl isopropylmalonate is treated with sodium ethoxide and ethyl α-bromisobutyrate, no corresponding reaction takes place, a mixture of high and low boiling substances being obtained.

H. G. C.

Dialkyl Cyanothiocarbamides. By O. Hecht (*Ber.*, **23**, 1658—1668; compare Wunderlich, Abstr., 1886, 435).—Methylthiocarbamide, in alcoholic solution, combines with sodium cyanide to form sodium methylcyanothiocarbamide, $NHMe{\cdot}CS{\cdot}NNa{\cdot}CN$; by the action of alkyl halogens, the sodium in this compound may be displaced. Since the higher thiocarbamides react in the same manner as the methyl compound, there is no difficulty in preparing the members of two homologous series, and a comparison of their properties would show the influence of the relative position of the alkyl-groups in the molecule.

I. Methylthiocarbamidealkyl Cyanides, $NHMe{\cdot}CS{\cdot}NR{\cdot}CN$.—*Methylthiocarbamidemethyl cyanide*, $NHMe{\cdot}CS{\cdot}NMe{\cdot}CN$, crystallises from alcohol in transparent, lustrous plates; on heating to 185°, it becomes yellow, and melts at 194—195° with decomposition; it is readily soluble in all the usual menstrua except light petroleum. *Methylthiocarbamidepropyl cyanide*, $NHMe{\cdot}CS{\cdot}NPr{\cdot}CN$, crystallises from hot water in very lustrous plates or needles melting at 90·5°;

it is less soluble than the methyl compound. *Methylthiocarbamideallyl cyanide*, NHMe·CS·N(C_3H_5)·CN, is deposited from alcohol in long, lustrous, white needles melting at 77·5°. *Methylthiocarbamidebenzyl cyanide*, NHMe·CS·N(C_7H_7)·CN, crystallises from hot alcohol in needles melting at 173°; it is only sparingly soluble in ordinary solvents.

II. ETHYLTHIOCARBAMIDEALKYL CYANIDES, NHEt·CS·NR·CN.—*Ethylthiocarbamideethyl cyanide*, NHEt·CS·NEt·CN, is obtained from sodium ethylcyanothiocarbamide and ethyl iodide; it crystallises from strong alcohol in white, lustrous laminæ melting at 98·2°, and resolidifying at 94°. *Ethylthiocarbamidepropyl cyanide*,

NHEt·CS·NPr·CN,

forms a loose, white, crystalline mass of small needles or leaves melting at 74·7° and resolidifying at 71°. *Ethylthiocarbamideallyl cyanide*, NHEt·CS·N(C_3H_5)·CN, crystallises in small, lustrous plates melting at 81·2° without decomposition. *Ethylthiocarbamidebenzyl cyanide*, NHEt·CS·N(C_7H_7)·CN, is deposited from dilute alcohol as a white powder, consisting of small, flat crystals melting at 143·5°.

III. PROPYLTHIOCARBAMIDEALKYL CYANIDES, NHPr·CS·NR·CN.—*Propylthiocarbamidemethyl cyanide* crystallises from alcohol in fine, white, lustrous plates melting at 115° without decomposition. *Propylthiocarbamideethyl cyanide* is obtained from hot water in plates melting at 56°. *Propylthiocarbamidepropyl cyanide* is deposited from hot water as a crystalline powder melting at 56°. *Propylthiocarbamideallyl cyanide*, crystallises in small, white, lustrous needles melting at 50·3°. *Propylthiocarbamidebenzyl cyanide* crystallises from hot water in needles melting at 113°.

IV. ALLYLTHIOCARBAMIDEALKYL CYANIDES, NH(C_3H_5)·CS·NR·CN.—Sodium allylcyanothiocarbamide is less soluble than the lower homologues, and the yield of alkyl-derivatives is comparatively small. *Allylthiocarbamideethyl cyanide* crystallises from dilute alcohol in fine, white needles melting at 63·2°. *Allylthiocarbamidepropyl cyanide* melts at 57·3°, and is deposited from dilute alcohol in small, lustrous needles. *Allylthiocarbamideallyl cyanide* forms fine, white, interlaced needles melting at 52·4°. *Allylthiocarbamidebenzyl cyanide* is difficult to purify; it is obtained from dilute alcohol in white, lustrous needles melting at 116° without decomposition.

V. PHENYLTHIOCARBAMIDEALKYL CYANIDES, NHPh·CS·NR·CN.—*Phenylthiocarbamidemethyl cyanide* is very sparingly soluble, except in acetic acid; it is deposited from a mixture of acetone and alcohol in white, lustrous, crystalline aggregates melting at 186° with decomposition. *Phenylthiocarbamideethyl cyanide* crystallises from water in white, interlaced needles and plates melting at 144°. Wunderlich (*loc. cit.*) gives the melting point of this compound as 119°. *Phenylthiocarbamidepropyl cyanide* melts under water; it is sparingly soluble, and separates as an oil, on cooling a hot solution; after remaining for some time, the oil solidifies, forming white, interlaced, needle-shaped crystals melting at 108°. *Phenylthiocarbamideallyl cyanide* is obtained in the form of slightly yellow, lustrous plates and needles melting at 100°. *Phenylthiocarbamidebenzyl cyanide* crystallises from a mixture

of acetone and alcohol in white, lustrous aggregates of needles and plates melting at 182° with decomposition. The melting points of the above compounds, except the allyl and aromatic derivatives, decrease with rising molecular weights; the position of the alkyl groups does not affect this rule. A comparison of the six pairs of metamerides shows that the compounds containing the group ·NMe·CN, have always the highest melting point; in the absence of a methyl-group, that metameride melts higher which has the alkyl of larger molecular weight linked to the :N·CN group. J. B. T.

Fucusol. By K. BIELER and B. TOLLENS (*Annalen*, **258**, 110—128; compare Abstr., 1890, 238; Maquenne, Abstr., 1890, 33; and Hill, Abstr., 1889, 695).—Fucusol, prepared from *Fucus* by distillation with sulphuric acid, can be separated by fractional distillation into furfuraldehyde and a much smaller fraction which consists of methylfurfuraldehyde (b. p. 182—184°). The furfuraldehyde was proved to be identical with that obtained from bran by a direct comparison of a number of derivatives of the two substances.

Methylfurfuraldehyde gives a deep orange-red coloration with aniline acetate.

Methylfurfurine, prepared by boiling the hydramide with soda, is an oil. The *nitrate* is crystalline. The acid *oxalate*, $C_{18}H_{16}N_2O_3,C_2H_2O_4$, crystallises in microscopic needles. The *platinochloride*,

$$(C_{18}H_{16}N_2O_3)_2,H_2PtCl_6,$$

crystallises in microscopic plates.

When a trace of isatin is added to a solution of methylpyromucic acid in concentrated sulphuric acid, and the mixture warmed slowly, a yellow, then a brown, and finally an intense green coloration is produced; in an aqueous solution of ammonium methyl pyromucate, ferric chloride produces a brown precipitate.

The authors have succeeded in extracting a sugar from *Fucus*, but have not yet obtained it in crystals. This sugar yields a crystalline *hydrazone*, melting at 163—165°, which seems to have the composition $C_{12}H_{18}N_2O_4$, and a crystalline *osazone*, melting at 154—156°; when distilled with dilute hydrochloric acid, it yields furfuraldehyde or methylfurfuraldehyde. F. S. K.

Configuration of the Benzene and Hexamethylene Molecule. By F. HERRMANN (*Ber.*, **23**, 2060—2062).—The author complains that Sachse (Abstr., 1888, 1181, and *Ber.*, **23**, 1363) has not noticed his (the author's) previous paper (Abstr., 1888, 1026) on the configuration of the benzene and hexamethylene molecule; he points out the similarity between his and Sachse's diagrams, and proceeds to discuss the conclusions which follow from the comparison.

F. S. K.

Chlorine Substitution-products of Metaxylene. By A. CLAUS and H. BURSTERT (*J. pr. Chem.* [2], **41**, 552—563).—Chlorine substitution-products of metaxylene are best obtained by slowly passing chlorine into a solution of metaxylene (100 grams) in chloroform (300 grams) containing finely powdered iron (6—7 grams). When

crystals begin to form in the liquid, the current of chlorine is stopped, and the product poured into water and shaken therewith; the chloroform solution is dried with calcium chloride, evaporated, and the residue distilled. Mono-, di-, and tri-chlorometaxylene distil over below 250°, and tetrachlorometaxylene remains. The first three are separated by fractional distillation, but the last cannot be distilled without decomposition; it may, however, be completely freed from the others by distillation with steam, with which it is not volatile.

Chlorometaxylene boils at 180—181° (uncorr.), not 186·5° (corr.; Jacobsen, Abstr., 1885, 1052).

4 : 6-*Dichlorometaxylene* crystallises in colourless, pearly, large plates; it strongly resembles dichloroparaxylene in properties, but its crystalline form is not so well marked; it melts at 68° (uncorr.), boils at 222°, and dissolves easily in most solvents, more sparingly in alcohol. The crystals have an aromatic odour, and become liquid when exposed for some time to the air; they sublime unchanged.

4 : 6-*Dichloro-3-methylbenzoic acid* is formed when 4 : 6-dichlorometaxylene (1 part) is heated with nitric acid of sp. gr. 1·18 (15 parts) in a sealed tube for 5—6 hours at 150°. It crystallises in colourless, lustrous needles which melt at 170° (uncorr.), and dissolve in hot water and the other usual solvents. It is not formed when chromic acid acts on 4 : 6-dichlorometaxylene in glacial acetic acid, so it is not identical with Hollemann's dichloromethylbenzoic acid (m. p. 161°, *Annalen*, **144**, 269); its *barium salt* (with 2 mols. H_2O) is described.

4 : 6-*Dichlorisophthalic acid* is the product of the action of chromic acid on 4 : 6-dichlorometaxylene; it is best obtained by heating the dichloroxylene (1 part) with nitric acid of sp. gr. 1·18 (20 parts) in a sealed tube for several hours at 220°, and crystallising the product from alcohol. It forms a white powder, consisting of small needles, and melts at 280° (uncorr.); it dissolves in the usual solvents except cold water, but its solution in hot water may be cooled to 0° without crystallising. Its *barium* (with 1 mol. H_2O), *silver*, *copper*, *lead*, *nickel*, and *cobalt* salts were obtained.

Trichlorometaxylene crystallises in colourless, lustrous needles which melt at 117° (uncorr.), and sublime unchanged. It dissolves freely in glacial acetic acid, benzene, ether, and chloroform, sparingly in alcohol; its constitution is uncertain. By oxidation either with nitric or chromic acid, it yields *trichlorisophthalic acid* only. This acid crystallises in slender needles which melt at 223° (uncorr.), and sublime; it is soluble in the usual solvents. The *barium* (with 5 mols. H_2O) and the *silver* salts are described.

Tetrachlorometaxylene crystallises from a mixture of chloroform and alcohol in brilliant, white, brittle needles which melt at 210° (uncorr.), and are soluble in most solvents except alcohol. All attempts to obtain an acid by oxidising tetrachlorometaxylene have failed.

A. G. B.

Action of Sulphuric Acid on Iodometaxylene. By H. HAMMERLICH (*Ber.*, **23**, 1634—1636).—Iodometaxylene [Me : Me : I = 1 : 3 : 4] is prepared by treating diazoxylidine sulphate with a concentrated solution of potassium iodide. The dark coloured oil which

collects at the bottom of the vessel is purified by washing with sodium hydroxide solution. After distilling several times, the compound is obtained as a colourless, strongly refractive liquid of sp. gr. 1·6609 at 13°; it boils at 232°, and does not solidify in a freezing mixture.

Diiodoxylene, $C_6H_2Me_2I_2$, is obtained by treating iodometaxylene with 2—3 times its weight of concentrated sulphuric acid. After remaining for about five weeks, the crystals which form are separated, and purified by washing and distillation. The compound crystallises from alcohol in tufts of long, white needles melting at 72°. On treating the acid filtrate from the diiodoxylene with barium carbonate, the barium salt of the corresponding *iodoxylenesulphonic acid* is obtained, crystallising in small, lustrous needles which are sparingly soluble in hot water.

Iodoisophthalic acid is formed by the oxidation of iodometaxylene with dilute nitric acid; the compound crystallises with great difficulty, and is best purified by treating the barium salt with hydrochloric acid; it melts at 215° with decomposition. The barium salt crystallises in small, white, lustrous needles. J. B. T.

Metadichlorophenol and Metadibromophenol. By L. GARZINO (*Chem. Centr.*, 1890, i, 820—821; from *Atti R. Acad. Sci., Torino*, **25**).—The author nitrated propionyldichlorophenols and propionyldibromophenols with the object of preparing monochloro- and monobromo-nitroquinones. Instead of these, a dinitrodichlorophenol and a dinitrodibromophenol were obtained.

Dinitrodichlorophenol, $C_6HCl_2(NO_2)_2{\cdot}OH$, forms yellow crystals melting at 105—106°, readily soluble in alcohol, ether, chloroform, and in hot water. It volatilises with steam, and decomposes when heated rapidly. It decomposes metallic carbonates in the cold. The *potassium salt* crystallises in red needles with $\frac{1}{2}$ mol. H_2O, and is very soluble in water. The *barium salt* crystallises with 3 and with 2 mols. H_2O. The former is yellowish, whilst the latter is reddish, and is less soluble in water.

By nitrating propionyldibromophenol without cooling, the principal product is dinitrodibromophenol, but if the mixture is carefully cooled during the nitration, a propionylnitrodibromophenol is also formed in some quantity.

Dinitrodibromophenol, $C_6HBr_2(NO_2)_2{\cdot}OH$, forms reddish-yellow crystals melting at 146° with decomposition. It is readily soluble in alcohol and ether, but little so in cold water, rather more soluble in hot water. From ether, it crystallises in beautiful rhombohedrons. It is volatile in steam, and decomposes metallic carbonates in the cold. The *potassium salt* crystallises with $\frac{1}{2}$ mol. H_2O in the form of dark-red needles little soluble in water. The *barium salt* crystallises with 3 and with 2 mols. H_2O in the form of small, red prisms.

Propionylnitrodibromophenol, $C_6H_2Br_2(NO_2)O{\cdot}C_3H_5O$, crystallises from dilute alcohol in beautiful, monoclinic crystals melting at 54—55°. By saponification, the nitrodibromophenol is obtained; it has a beautiful, yellow colour, and melts at 90—91°. The positions of the nitro-groups in these compounds is not determined. J. W. L.

Chlorodibromo- and Bromodichloro-phenol, and their Conversion into Quinones. By L. GARZINO (*Chem. Centr.*, 1890, i, 821; from *Atti R. Acad. Sci., Torino*, **25**).—*Chlorodibromophenol*, $C_6H_2Br_2Cl{\cdot}OH$ [= 2 : 4 : 5 : 1 ?], is prepared by treating metadibromophenol with dry chlorine at 40°. It crystallises from dilute alcohol in white, silky, lustrous crystals, very soluble in ether, chloroform, and benzene, soluble in dilute acetic acid, nearly insoluble in water; it is volatile with steam, and sublimes at ordinary temperatures. The *barium salt* crystallises with $2\frac{1}{2}$ mols. H_2O in small, yellowish-white needles; the aqueous solntion is decomposed partially by evaporation; it is not readily soluble in water. *Benzoylchlorodibromophenol*, $C_6H_2Br_2Cl{\cdot}OBz$, forms small, white prisms, and melts at 65—65·5°.

Propionylchlorodibromophenol, $C_6H_2Br_2Cl{\cdot}O{\cdot}C_3H_5O$, crystallises from 80 per cent. alcohol in white crystals melting at 31·5—32°. By nitrating this, *chlorobromonitroquinone* is obtained in small quantity; it decomposes at its melting point, 227—228°; it is insoluble in water, sparingly soluble in ether, insoluble in cold 95 per cent. alcohol, and but little soluble in hot alcohol; this solution becomes brown and acid. It reacts with hydroxylamine hydrochloride, phenylhydrazine, and aniline. On nitrating the propionylbromodichlorophenol, no quinone is obtained; a propionyl-derivative of nitrobromodichlorophenol and a substance of the formula $C_{12}H_4Cl_3BrN_2O_7$, but whose constitution could not be determined, were obtained. The latter melts at 215—217°. The propionylnitrobromodichlorophenol melts at 88·5—89°, is sparingly soluble in water, and crystallises from boiling alcohol in greenish-white rhombohedra. J. W. L.

Action of Bromine on Phloroglucinol. By T. ZINCKE and O. KEGEL (*Ber.*, **23**, 1706—1732).—By the action of bromine on phloroglucinol, Benedikt (Abstr., 1878, 499; *Jahresb.*, 1880, 645), and Benedikt and Hazura (Abstr., 1886, 52) obtained three compounds, phlorobromine, C_6Br_9HO: hexabromophloroglucinol, $C_6Br_6O_3$; and octobromophloroglucinol, $C_6Br_8O_3$. The observations made by the authors in their investigation of the action of chlorine on phloroglucinol (this vol., p. 488) have induced them to repeat these experiments, and it has been found that phlorobromine has not the formula C_6Br_9HO, but $C_5Br_8O_2$, and is in reality *perbromacetylacetone*, $CBr_3{\cdot}CO{\cdot}CBr_2{\cdot}CO{\cdot}CBr_3$. It forms thick, lustrous needles which melt at 154—155°, and give off bromine at a higher temperature. It dissolves sparingly in light petroleum, but readily in benzene, chloroform, and acetic acid, and is not attacked by soda solution or by nitric acid. Ammonia converts it into tribromacetamide and methylene bromide, whilst with alcohol it yields bromoform and ethyl di- and tri-bromacetate.

The formation of perbromacetylacetone is probably preceded by that of hexabromophloroglucinol, which is then acted on by bromine-water in the following manner:—

$$\begin{array}{l}CO{\cdot}CBr_2{\cdot}CO\\ |\qquad\qquad\quad |\\ CBr_2{\cdot}CO{\cdot}CBr_2\end{array} + 2Br_2 + 2H_2O = \begin{array}{l}CO{\cdot}CBr_3 + CO_2\\ |\\ CBr_2{\cdot}CO{\cdot}CBr_3\end{array} + 2HBr.$$

From this, one would expect that tribromophloroglucinol would yield by the action of chlorine the compound $CCl_2Br{\cdot}CO{\cdot}CBrCl{\cdot}CO{\cdot}CCl_2Br$,

and that trichlorophloroglucinol would form with bromine the compound $CBr_2Cl{\cdot}CO{\cdot}CBrCl{\cdot}CO{\cdot}CBr_2Cl$. The latter supposition has proved correct, but not the first, as in that case the pentabromo-compound is also formed, together with compounds richer in chlorine. It appears probable that, on the one hand, the mixed trichlorotribromotriketohexamethylene is formed; whilst, on the other, bromine is set free, which then acts on the first-named compound, forming pentabromotrichloracetylacetone. This compound forms hard, colourless, vitreous needles which melt at 93—95° to a milky liquid which becomes clear at 98°. It is soluble in the ordinary solvents, the solutions quickly undergoing decomposition. Ammonia converts it into dibromochloracetamide, which forms thick, colourless needles or broad plates melting at 127—128°.

By the action of bromine on phloroglucinol in concentrated aqueous solution, the authors have not been able to obtain Benedikt's octobromophloroglucinol, but have isolated hexabromophloroglucinol and a new compound having the composition $C_5Br_7HO_2$. If the bromination be incomplete, a compound $C_6H_3Br_5O_4$ or $C_6Br_5HO_3,H_2O$ is also obtained.

Both this compound and the hexabrominated derivative are much more stable than the corresponding hexachlorotriketohexamethylene, not being split up by water, alcohol, or ammonia.

Hexabromotriketohexamethylene forms large, well-developed tablets, which are colourless or slightly yellow, melt at 146—147°, and decompose at 170—180°. It is readily soluble in ether, chloroform, hot benzene, and hot acetic acid, and is exceptionally susceptible to light. On reduction, it yields tribromophloroglucinol, and, under favourable conditions, phloroglucinol. Bromine converts it into phlorobromine.

The second compound, $C_6Br_5HO_3,H_2O$, is probably a *pentabromodiketohydroxyhexene*, $\begin{array}{l} CBr{\cdot}CO{\cdot}CBr_2 \\ \parallel \qquad\quad\;\; | \\ HO{\cdot}C \cdot CBr_2{\cdot}CO \end{array}$,$H_2O$, as it yields an acetyl-derivative, $C_6Br_5O_2{\cdot}OAc$, by the action of acetic anhydride with elimination of 2 mols. of water. This, on reduction and further treatment with acetic anhydride, yields *tribromophloroglucinol triacetate*, $C_6Br_3(OAc)_3$. The first-named compound forms slender needles melting at 142°, whilst the second melts at 183—184°.

Pentabromodiketohydroxyhexene crystallises in transparent, amber-yellow, apparently monoclinic forms, which are easily soluble in water and ether, less readily in chloroform and acetic acid. It melts at 119—120° with decomposition, and does not lose its water of crystallisation without further decomposition. This is probably combined in the same manner as in mesoxalic acid, which would account for the solubility of the compound in water. It behaves on reduction in the same manner as the hexabromo-componnd, and by the action of bromine yields the compound $C_5Br_7HO_2$, which, as already stated, is also obtained direct from phloroglucinol. It crystallises from a mixture of carbon bisulphide and light petroleum in colourless, monoclinic prisms which melt at 93—94°, and give off bromine at a higher temperature. It greatly resembles phlorobromine, and by the action of water yields pentabromacetone, and a compound which is possibly tetrabromacetone hydrate. Ammonia converts it into tribromacet-

amide. From these facts, it would appear that the compound is a *heptabromacetylacetone* having the constitution

$CBr_3 \cdot CO \cdot CBr_2 \cdot CO \cdot CBr_2H$. H. G. C.

Methyl-derivatives of Phloroglucinol. By A. SPITZER (*Monatsh.*, **11**, 104—119).—The methyl-derivatives of phloroglucinol may be obtained in satisfactory yield and in unvarying proportions if the methyl iodide and phenol are both perfectly dry, and if in their preparation sodium be substituted for potassium. The phloroglucinol (1 mol.), dried at 100°, and the sodium (6 atoms) are separately dissolved in absolute methyl alcohol, the solutions are mixed, and the methyl iodide (6 mols.) run in, drop by drop, from a funnel. The mixture is then heated in a reflux apparatus, so arranged as to exclude moisture, until it no longer gives an alkaline reaction. The remainder of the operation is carried out in accordance with the directions of Herzig and Zeisel (Abstr., 1888, 822). On treating the product with dilute aqueous potash, hexamethylphloroglucinol and an oily portion remain undissolved, whilst penta- and tetra-methylphloroglucinol and a product not yet investigated are soluble in it.

Hexamethylphloroglucinol showed the same melting point (80°) as given by Margulies, and boiled at 247·7° (corr.). On treating the compound with hydrogen iodide, Margulies obtained carbonic anhydride, isobutyric acid, and diisopropylmethane, the latter being presumably secondary products from dimethylmalonic acid and diisopropyl ketone, which would decompose under the influence of the reducing agent at the high temperature (200°) employed. To test the truth of this supposition, the author has made experiments substituting 40 per cent. hydrochloric and 50 per cent. sulphuric acids for the hydrogen iodide. On heating the mixtures in sealed tubes at 190°, carbonic anhydride, diisopropyl ketone, and a small quantity of isobutyric acid were simultaneously formed.

Pentamethylphloroglucinol.—This compound melts at 114°, and boils at 261·6—263·8° (corr.), and has been described under the name of tetramethylphloroglucinol by Margulies. When an alcoholic solution is treated with bromine, *monobromopentamethylphloroglucinol*, crystallising in beautiful, small, white needles, is obtained; it melts at 75—76°. On heating for several hours in a reflux apparatus with 1 per cent. sodium hydroxide, this compound gradually dissolves, and on distilling the product, an oil boiling at 123·7—126·5° (corr.) passes over. This oil is diisopropyl ketone, since, on oxidation, it gives a mixture of acetic and isobutyric acids. On heating pentamethylphloroglucinol (2 grams) with 20 per cent. hydrochloric acid (20 c.c.) at 180° in a sealed tube, isobutyric, propionic, and carbonic acids, diisopropyl ketone, and perhaps ethyl isopropyl ketone are formed.

Since the action of bases on the brominated pentamethylphloroglucinol indicates the existence of symmetrical tetramethylacetone, and since its hydroxylic character has been established, the constitution of pentamethylphloroglucinol must be expressed by the formula

$$OH \cdot C {\lessgtr}^{CMe_2 \cdot CO}_{CMe \cdot CO} {>} CMe_2.$$

On oxidation with atmospheric air, four of the methyl-groups of pentamethylphloroglucinol are converted into diisopropyl ketone, and the fifth into acetic acid. It may be supposed that in this action the double-bonded carbon-atoms are split asunder, and the free valencies occupied by oxygen, the compound

$$COOH\cdot CMe_2\cdot CO\cdot CMe_2\cdot CO\cdot COMe$$

being formed, and that this hypothetical triketonic acid, in presence of water and oxygen, is finally split up into carbonic anhydride, acetic acid, and tetramethylacetone. G. T. M.

Homofluoresceïn. By E. GRIMAUX (*Compt. rend.*, **110**, 1074—1076).—The sodium-derivative of homofluoresceïn, prepared by Schwarz's method (Abstr., 1880, 551), was twice recrystallised from acetic acid. At 100°, the crystals lost 31·3 per cent. of acetic acid; Schwarz's product lost 31·55 per cent.

Orcin-aurin, prepared by Nencki's process (Abstr., 1882, 1201), was also crystallised from acetic acid; the crystals lost 32·2 per cent. at 100°.

Both products had precisely the same appearance, and formed needles, with a brown-red kermes-like colour, which did not melt at 300°. When heated in small closed tubes, they melt and decompose with evolution of red vapours and formation of a carbonaceous residue. With barium hydroxide solution, they yield a red, crystalline precipitate of a barium salt, very slightly soluble in cold water, but soluble in boiling water; with nitric acid, they yield nitro-derivatives which crystallise from water in rhombic lamellæ; and with alkalis, they yield two compounds which have the same intense fluorescence.

The homofluoresceïn of Schwarz is, in fact, identical with the orcin-aurin of Nencki. The formula $C_{22}H_{18}O_5$ agrees better with the properties described by Schwarz and with his analyses of the nitro-derivatives than does the formula $C_{23}H_{16}O_5$, which he ascribed to the compound.

Resorcinol, when treated with chloroform and an alkali, yields a bright-red, non-fluorescent solution which becomes brown-red on prolonged boiling. Acids precipitate a yellow powder which should be identical with the resaurin obtained by Nencki by heating resorcinol with formic acid and zinc chloride at 140°. Resorcinphthaleïn is fluorescent, and orcinphthaleïn is non-fluorescent, but the reverse holds good for the products of the action of chloroform.

C. H. B.

The Phenol contained in Sassafras Oil. By C. POMERANZ (*Monatsh.*, **11**, 101—103).—According to Grimaux and Ruott (*Compt. rend.*, **68**, 928), the ethereal oil obtained from the American cinnamon-tree, *Laurus sassafras*, consists of 10 per cent. of a terpene $C_{10}H_{16}$, 90 per cent. of safrole, $C_{10}H_{10}O_2$, and a small quantity of a substance of a phenolic nature, which can be abstracted from the oil by shaking with potash. In order to further investigate it, the author has exhausted 3 kilos. of crude sassafras oil with dilute potash. On adding dilute sulphuric acid to the alkaline solution, an oil separated; this was washed, dried with calcium chloride, and distilled. The whole

of the oil passed over between 246° and 247°, giving 7 grams of a colourless liquid, having an odour greatly resembling eugenol. It is heavier than water, in which it is nearly insoluble, and dissolves readily in alcohol, forming a solution which is turned blue by ferric chloride. All these properties agree perfectly with those of eugenol, $OH·C_6H_3(OMe)·C_3H_5$. The elementary analysis and the conversion of a portion of the substance into its characteristic benzoyl-derivative (compare Cahours, *Annalen*, **108**, 321), crystallising in colourless, gleaming prisms melting at 69°, show that the substance is, in fact, eugenol. G. T. M.

Action of Zinc Chloride on Methylacetanilide. By A. Pictet and J. Fert (*Ber.*, **23**, 1903—1904; compare Abstr., 1889, 971).—Methylacetanilide is heated with zinc chloride at 290° for some time; when no further evolution of gas occurs, the fused mass is poured into dilute hydrochloric acid, excess of alkali added, and the solution extracted with ether; on evaporation of the ether, an oily residue is obtained consisting chiefly of quinoline and paratoluidine. The decomposition of methylacetanilide is therefore strictly analogous to that of ethylacetanilide. J. B. T.

Isomerism of Organic Substances containing Nitrogen. By L. Gattermann (*Ber.*, **23**, 1733—1737).—Nitroparacetyltoluide, $CH_3·C_6H_3(NO_2)·NHAc$ (1 . 3 . 4), can be obtained in two modifications, one of which is yellow and the other white, according as it is crystallised from water or alcohol. These two modifications readily pass into one another under various conditions. Thus the white variety is converted into the yellow compound a few degrees below its melting point, and either modification can be obtained at will by adding a crystal of the one required to the melted substance. The butyryl compound behaves, according to Broemme, in a similar manner. Another compound, closely related to the foregoing, acetylazimidotoluene, also exists in two similar forms (Bössneck, Abstr., 1886, 874; Zincke and Lawson, *Annalen*, **240**, 119); and the author and Ritschke, in their investigation of azoxyphenol ethers, find that a yellow and a white modification of parazoxyanisoïl can also be obtained.

To determine whether we have here to do with a case of physical or chemical isomerism, or with an example of stereometrically isomeric nitrogen compounds, further investigation is necessary.

H. G. C.

Anilides and Toluidides of Tartaric Acid. By C. A. Bischoff and O. Nastvogel (*Ber.*, **23**, 2047—2051).—An amorphous compound, which seems to have the composition C_6H_5NO, is formed, together with tartranilic acid and various amorphous substances, when acid aniline tartrate is heated; it softens and decomposes at 200—225°, but without melting, and it is readily soluble in alcohol and glacial acetic acid, but only sparingly in benzene.

Tartaric diorthotoluidide, $C_{18}H_{20}N_2O_4$, is obtained when orthotoluidine tartrate (m. p. 151—152°) is heated with orthotoluidine at 160°; it crystallises from dilute alcohol in plates, melts at 182—183°, and is

readily soluble in hot acetone, xylene, glacial acetic acid, and alcohol, but only sparingly in hot benzene, chloroform, and carbon bisulphide, and almost insoluble in ether and water. The *diacetyl*-derivative, $C_{22}H_{24}N_2O_6$, is formed when the ditoluidide is heated at 135—140° with acetic anhydride; it melts at 221—222°, and resembles the ditoluidide in its behaviour with solvents.

Tartaric diparatoluidide, $C_{18}H_{20}N_2O_4$, prepared from acid paratoluidine tartrate (m. p. 198° with decomposition), crystallises from hot alcohol in colourless needles, and melts at 264° with decomposition. The *diacetyl*-derivative, $C_{22}H_{24}N_2O_6$, separates from alcohol in crystals and melts at 202°. F. S. K.

Orthonitrodiphenylamine. By M. SCHÖPFF (*Ber.*, 23, 1839—1844; compare Abstr., 1889, 772).—An increased yield of orthonitrodiphenylamine is obtained by preparing it from orthobromonitrobenzene, instead of orthochloronitrobenzene, aniline or glycerol being used as a solvent in place of alcohol. The result is still more satisfactory if the orthobromonitrobenzene is first sulphonated and then treated with aniline, nitranilidobenzenesulphonic acid [$NO_2 : NHPh : SO_3H = 1 : 2 : 5$] is formed, and on heating with hydrochloric acid in a sealed tube, it is converted, almost quantitatively, into orthonitrodiphenylamine. All attempts to prepare an acetyl-derivative of orthonitrodiphenylamine were fruitless.

Orthonitrophenylparamidotoluene, $NO_2\cdot C_6H_4\cdot NH\cdot C_6H_4Me$ [$NH : NO_2 = 1 : 2$; $NH : Me = 1 : 4$], is obtained by heating orthobromonitrobenzene with excess of paratoluidine, the product is poured into dilute hydrochloric acid, and purified by distillation in a current of steam. The compound melts at 68°, and resembles the aniline-derivative in appearance. Experiments with the naphthylamines were unsuccessful, and no satisfactory results were obtained with bromonitrotoluene [$Me : NO_2 : Br = 1 : 3 : 4$].

Orthamidodiphenylamine, $NH_2\cdot C_6H_4\cdot NHPh$, is prepared by heating the nitro-compound with alcoholic ammonium sulphide in a sealed tube for four hours at 120°; the alcohol is evaporated, the residue treated with hydrochloric acid, boiled, filtered, and the base precipitated with ammonia. The compound crystallises from water in colourless needles melting at 79—80°; it is readily soluble in benzene, chloroform, and acetone, but less so in light petroleum; it is identical with the substance obtained from anilidoamidobenzoic acid [$COOH : NH_2 : NHPh = 1 : 3 : 4$] by distillation. The *hydrochloride* is prepared by adding concentrated hydrochloric acid to a solution of the base in dilute acid; it crystallises in needles, and gives a dark red coloration with ferric chloride; the same coloration is produced on exposure to air of an aqueous solution of the hydrochloride.

Orthophenylazimidobenzene, $C_6H_4<\genfrac{}{}{0pt}{}{N:N}{NPh}>$, is obtained by the action of sodium nitrite on orthamidodiphenylamine dissolved in excess of dilute hydrochloric acid; the precipitate which forms is dissolved in alcohol, water is added, and after some time reddish needles are deposited, melting at 89—90°. This compound is isomeric with the substance obtained by Gattermann and Wichmann (compare Abstr.,

1888, 829) from aniline and diazoamidobenzene. From its constitution, and the manner of its formation, Gattermann's compound should be called phenylpseudoazimidobenzene. J. B. T.

Derivatives of Diphenylamine and Phenazine. By R. NIETZKI and O. ERNST (*Ber.*, 23, 1852—1856).—Toluylene-blue, $C_{15}H_{18}N_4$, has been shown to belong to the group of indamine dyes; it is prepared by the action of nitrosodimethylamine on diamidotoluene [$Me:NH_2:NH_2 = 1:2:4$]. Toluylene-red, $C_{15}H_{16}N_4$, which is formed from toluylene-blue by the action of heat, is known to be an amidoazine (eurhodine). Since the indamines are derived from amidodiphenylamine, the leuko-base of toluylene-blue should have the formula $C_6H_2Me(NH_2)_2\cdot NH\cdot C_6H_4\cdot NMe_2$ [$NH:(NH_2)_2:Me = 1:2:4:5$; $NH:N = 1:4$], and the simplest analogue would be triamidodiphenylamine, $C_6H_3(NH)_2\cdot NH\cdot C_6H_4\cdot NH_2$ [$NH:(NH_2)_2 = 1:2:4$; $NH:NH_2 = 1:4$].

Dinitramidodiphenylamine, $C_6H_3(NO_2)_2\cdot NH\cdot C_6H_4\cdot NH_2$, is prepared from dinitrochlorobenzene [$Cl:(NO_2)_2 = 1:2:4$] and paradiamidobenzene by warming the alcoholic solution. The compound crystallises from benzene or chloroform in small, brownish-red leaves, having a metallic sheen, and melting at 177°; it is sparingly soluble in alcohol, and has tolerably well marked basic properties. The *hydrochloride* forms slightly yellow needles. The *picrate*,

$$C_{12}H_{10}N_4O_4,C_6H_2(NO_2)_3\cdot OH,$$

crystallises in brown needles. On warming with acetic anhydride, the *monacetyl*-derivative is obtained, crystallising in ruby-red needles melting at 238°; the same compound may also be prepared by the action of dinitrochlorobenzene on monacetylparadiamidobenzene.

Diacetyldinitroamidodiphenylamine is formed by boiling the dinitro-compound for some time with acetic anhydride; it crystallises in brownish-yellow plates.

Triamidodiphenylamine hydrochloride is prepared by reducing the dinitro-compound with stannous chloride and hydrochloric acid, the stannochloride is precipitated by saturating with gaseous hydrogen chloride, and the tin eliminated with hydrogen sulphide; the compound crystallises in flat needles, which speedily become blue-violet on exposure to air. The *sulphate* crystallises in colourless, lustrous needles. A violet-blue compound is obtained by the oxidation of these salts, and although somewhat unstable, it still shows all the characteristic properties of the indamine dyes, and is undoubtedly the analogue of toluylene-blue.

2 . 2-*Diamidophenazine*, $C_{12}N_2H_6(NH_2)_2$, is prepared by boiling triamidodiphenylamine stannochloride with calcium carbonate and manganese dioxide. After filtration, the solution is treated with a little hydrochloric acid, and the hydrochloride precipitated with sodium chloride. The free base is obtained by the action of ammonia; it crystallises from water in dark yellow needles melting at 280°; the alcoholic and ethereal solutions are strongly fluorescent; with concentrated sulphuric acid, it gives a green coloration, which changes successively to blue, violet, and red on adding water. All the salts are red in solution. The *nitrate*, $C_{12}H_{10}N_4,HNO_3$, crystallises in greenish,

lustrous needles. The *picrate* forms needles having a brownish sheen. The *platinochloride*, $(C_{12}H_{10}N_4)_2,H_2PtCl_6 + H_2O$, is obtained as a fine crystalline precipitate, with a yellowish-green lustre.

Diacetyldiamidophenazine is prepared by heating diamidophenazine with acetic anhydride and acetic acid; it crystallises from dilute alcohol in yellow needles melting at 330°, and gives, with concentrated sulphuric acid, a red colour, which changes to yellow on adding water; if this solution is boiled, the acetyl-groups are eliminated.

The salts of diamidophenazine dye silk red; the tint is yellower than that obtained from the simpler saframines, but the dye can be of no technical importance on account of the yellow shade which is produced by relatively small quantities of alkalis.

Diamidophenazine may also be obtained by the oxidation of para- and meta-diamidobenzene, or by the action of qninonedichlorimide on meta-diamidobenzene. Phenazine is formed by treating diamidophenazine with sodium nitrite and dilute sulphuric acid. J. B. T.

Diacetylorthodiamines. By A. BISTRZYCKI and F. ULFFERS (*Ber.*, **23**, 1876—1880); compare this vol., p. 969).—The following compounds have been prepared in addition to those already described; they are obtained by boiling the diamine (1 mol.) with the anhydride (3—4 mols.) for a few minutes; solid anhydrides may be dissolved in boiling benzene.

Diacetylorthophenylenediamine, $C_6H_4(NHAc)_2$, is deposited from water in long, slender, lustrous needles, or in thick crystals, melting at 185—186; it is readily soluble in water, alcohol, chloroform, acetone, and glacial acetic acid, but more sparingly in ether, benzene, and light petroleum. Dibenzoylorthophenylenediamine,

$$C_6H_4(NHBz)_2,$$

has already been prepared by a different method. *Diacetylorthodiamidotoluene*, $C_6H_3Me(NHAc)_2$ [Me : NHAc : NHAc = 1 : 3 : 4], is obtained from hot water in long, slender prisms melting at 210°; it resembles the phenylene compound in solubility; on distillation at ordinary pressure, it is converted into ethenyltoluyleneamidine. *Dipropionylorthodiamidotoluene*, $C_6H_3Me(NH{\cdot}COEt)_2$, crystallises from water in long, flat needles melting at 133°; it is very sparingly soluble in the ordinary menstrua. *Propenyltoluyleneamidine*, $C_6H_3{<}^{NH}_{N}{\gg}CEt$, is obtained in small quantity by distilling dipropionyldiamidotoluene under a pressure of 84 mm.; the distillate is dissolved in alcohol and the amidine precipitated with ammonia. It crystallises from dilute alcohol in characteristic interlaced needles melting at 166°. *Dicinnamylorthodiamidotoluene*, $C_6H_3Me(NH{\cdot}CO{\cdot}C_8H_7)_2$, is deposited from dilute alcohol in small, concentric needles, melting at 205—206° with previous softening. 1 . 2-*Dipropionylnaphthylenediamine*, $C_{10}H_6(NH{\cdot}COEt)_2$, crystallises from alcohol in fine prisms melting at 191—192; it is insoluble in ether and light petroleum. J. B. T.

Diazobenzene: a Correction. By T. SANDMEYER (*Ber.*, **23**, 1880—1881).—The author refers to the papers of L. Gattermann and of G. Tobias (compare this vol., pp. 970, 1149), and points out that, owing

to a printer's error in his original paper (compare Abstr., 1884, 1311), the word "water" was omitted from the description of the process for the preparation of diazobenzene chloride. J. B. T.

Intramolecular Transformation between a Diazo-salt-group and a Phenol-residue. By E. LELLMANN and H. BOYE (*Ber.*, **23**, 1781—1783).—Orthonitrobenzyl chloride (1 mol.) was heated with ethylmetamidophenol (2 mols.) in alcoholic solution on the water-bath, the alcohol was then distilled off, and the residual oil extracted repeatedly with water to remove ethylamidophenol hydrochloride. The residue was treated with dilute hydrochloric acid, and a grey, crystalline powder of the *hydrochloride* of *orthonitrobenzylethylmetamidophenol*, $HO\cdot C_6H_4\cdot NEt\cdot CH_2\cdot C_6H_4\cdot NO_2,HCl$, was obtained. This was reduced by dissolving it in strong hydrochloric acid, and allowing the solution to remain with rather more than the calculated quantity of stannous chloride. The greater part of the hydrochloric acid was then evaporated, the residue diluted with much water, cooled, and poured into a cold solution of ammonium sulphide; *orthamidobenzylethylmetamidophenol*, $HO\cdot C_6H_4\cdot NEt\cdot CH_2\cdot C_6H_4\cdot NH_2$, then separated in small, brilliant, nearly colourless plates, which after recrystallisation from ether melted at 145°. It was dissolved in dilute hydrochloric acid and heated with sodium nitrite (1 mol.); the solution turned brown. After remaining for 24 hours, the colouring matter was precipitated by adding sodium acetate, and when dried formed a dark-brown powder with a green fluorescence. It may be called *azobenzylethylamidophenol* or *azoxyethylbenzylaniline*, as it has the constitution $HO\cdot C_6H_3{<}{\substack{N{=\!=}N\\ NEt\cdot CH_2}}{>}C_6H_4$ [N : NEt : OH = 1 : 2 : 4, N : CH_2 = 1 : 2]; probably the diazochloride, $HO\cdot C_6H_4\cdot NEt\cdot CH_2\cdot C_6H_4NNCl$, is formed as a stage in the reaction. It behaves like an azo-colouring matter, and dyes silk a yellowish-brown which is hardly altered by acids or alkalis. It is decolorised by reducing agents, and dissolves easily in alcohol, acetic acid, and phenol. C. F. B.

Reduction of Nitro-azo-compounds by Alcoholic Ammonium Sulphide. By C. WILLGERODT (*J. pr. Chem.* [2], **42**, 49—56). —*Dihydroparadinitro-azobenzene* has been obtained by the author from paradinitro-azobenzene (m. p. 215—220°) by the action of alcoholic ammonium sulphide; it melts at 248—250°, but by recrystallisation the melting point falls, owing to decomposition; the compound obtained by Lermentoff (this Journal, 1872, 503), and called dinitro-hydrazobenzene by him and by Janovsky (Abstr., 1885, 789), is undoubtedly identical with it, notwithstanding that Lermentoff gives the melting point as 220°. Janovsky (*loc. cit.*) describes a nitro-azo-benzenenitrolic acid (m. p. 218°), which gives very similar reactions to the author's dihydroparadinitro-azobenzene. By carefully following Janovsky's directions, the author has failed to obtain this nitrolic acid, but has always obtained dihydroparadinitro-azobenzene; he, therefore, concludes that all these three substances are identical.

When ortho- or paranitro-azobenzene is shaken with alcoholic ammonium sulphide, and the solution precipitated by water, the corre-

sponding azoxybenzenes (m. p. 212°, uncorr.) are obtained; they are very similar to each other, and are identical with Janovsky's hexazoxybenzene (Abstr., 1886, 794). When the precipitated azoxybenzene is dissolved in alcohol, precipitated by water, and dried over calcium chloride, a compound, $O<\begin{matrix}NH(OH)\cdot C_6H_4\cdot N_2Ph\\ |\\ NH(OH)\cdot C_6H_4\cdot N_2Ph\end{matrix}$, is obtained. When an ethereal solution of the azoxybenzene is mixed with alcoholic platinic chloride, a *platinochloride*, $ON_2(PhN_2\cdot C_6H_4)_2,H_2PtCl_6$, is produced. When the compound precipitated by water from alcoholic solution (see above) is further dried at 40—50° over calcium chloride, an azohydroxyazobenzene, $PhN_2\cdot C_6H_4\cdot NOH$ (Janovsky's nitrolic acid), is obtained; a *platinochloride* thereof is described. A. G. B.

Isomeric Hydrazones of Orthonitrophenylglyoxylic Acid. By H. C. Fehrlin (*Ber.*, **23**, 1574—1587).—When the hydrazones of phenylglyoxylic acid, acetophenone, and benzaldehyde are heated with either aqueous or alcoholic potash, and sulphuric acid added to the solution, the original substance is regenerated, and the same is the case with the hydrazone of metanitrophenylglyoxylic acid; but orthonitrophenylglyoxylic acid hydrazone, though not acted on by aqueous potash, is converted, even in the cold, by alcoholic potash into an isomeric compound, which is precipitated by the addition of acids.

Metanitrophenylglyoxylic acid hydrazone was obtained by adding an acetic acid solution of phenylhydrazine to an aqueous solution of the acid. It crystallises from glacial acetic acid in transparent, yellow, quadrangular plates which melt with decomposition at 174—175°. It yields no isomeric compound when treated with potash.

Orthonitrophenylglyoxylic Acid Hydrazone.—The acid was prepared by Claissen and Shadwell's method, the improvements introduced being described in detail. Orthonitrobenzoyl chloride was heated for 24 hours 100° in a sealed tube with silver cyanide. The contents of the tube were extracted with ether, and the oil (cyanide) left after evaporating the ether was shaken with fuming hydrochloric acid, and allowed to remain; in three to four hours it was converted into the amide, which, after recrystallisation from benzene, melted at 199° (if from water, at 192°). This was dissolved in water and heated with potash until a slight smell only of ammonia could be perceived; the solution was then acidified, when orthonitrophenylglyoxylic acid was obtained as a brownish oil, solidifying to groups of small, colourless needles, which melted at 49°. The acid was dissolved in water, phenylhydrazine dissolved in acetic acid was added, and the hydrazone obtained by concentrating the solution. When recrystallised from alcohol, it forms transparent, red crystalline aggregates; from acetic acid, it crystallises in small, yellow, transparent tables; it melts with decomposition at 165—166°. When treated with an alcoholic alkaline solution, it is converted into an isomeric compound, which separates as a yellow precipitate when the solution is acidified, and crystallises from alcohol in brilliant, golden needles melting with decomposition at 189—190°, and becoming superficially green when exposed to light. A saturated solution in acetic acid (sp. gr. 1·06) contains at 19° and 20°, 1·06 and 1·24 parts of the hydrazone, and

0·24 and 0·28 parts of the isomeride. Both are insoluble in water and light petroleum, and nearly so in benzene, but dissolve in alcohol, ether, and acetic acid, the isomeride less readily. They are not acted on by dilute acids or strong hydrochloric acid; in concentrated sulphuric acid they give yellow solutions, which yield a resinous product when diluted with water. The original hydrazone dissolves easily in strong nitric acid, and on pouring the solution into water, yellow crystals are obtained, melting at 77—80°. The isomeric compound dissolves with difficulty, and only when the solution is heated; the product melts at 98—100°. Both these compounds give unstable, purple solutions with alkalis, and an unstable, deep-violet substance when treated with gaseous ammonia. The hydrazone is easily soluble in aqueous alkalis, the isomerides only with difficulty; the addition of an acid reprecipitates the substance in both cases.

Orthophenylglyoxylic acid methylhydrazone was prepared as above, using methylphenylhydrazine instead of phenylhydrazine; it separates out when the solution is warmed, and crystallises from alcohol in reddish-yellow needles melting at 141—142°. It forms no isomeric compound when treated with alkalis. With strong nitric acid, it yields a deep blue-green solution; with strong sulphuric acid, a violet solution.

The fact that the two hydrazones of orthonitrophenylglyoxylic acid give different compounds when treated with strong nitric acid, shows that they are chemically, and not merely physically, isomeric. And that the isomerism is due to a change in place of the hydrogen-atom of the hydrazone-group is shown by the methylhydrazone yielding no isomeride. The following two formulæ are therefore proposed:—

$$NHPh\cdot N:C(COOH)\cdot C_6H_4\cdot NO_2. \qquad \begin{matrix} NH- \\ | \\ NPh \end{matrix}\!\!>C(COOH)\cdot C_6H_4\cdot NO_2.$$

The hydrazone (165—166°). The isomeride (189—190°).

These are to some extent supported by the fact that the two substances appear to behave in the same manner when reduced, both yielding a yellow product of amido-oxindol. C. F. B.

Azohydrazine and Polyazo-compounds. By C. WILLGERODT (*J. pr. Chem.* [2], 41, 563—565).—The author and his pupils have obtained the following compounds by methods which will be fully detailed in a future communication.

Picrylparachlorophenylhydrazine.—This occurs in two modifications; the *red* variety crystallises in slender, reddish-yellow prisms which melt with decomposition at 170—175°; the *yellow* variety crystallises in very small, transparent, yellow needles which melt with decomposition at 176°, and are unstable, being converted into the red variety by heating with alcohol. Long digestion with alcohol converts both varieties into *dinitrosonitroparachlorazobenzene*,

$$C_6H_4Cl\cdot N_2\cdot C_6H_2(NO)_2\cdot NO_2,$$

melting at 199—200°. Similar treatment with glacial acetic acid converts them into *dinitronitrosoparachlorazobenzene*, melting at 241—242°, whilst oxidation with chromic acid converts them into *trinitroparachlorazobenzene*, $C_6H_4Cl\cdot N_2\cdot C_6H_2(NO_2)_3$, melting at 138—139°.

Tetranitroparachlorazobenzene, $NO_2{\cdot}C_6H_3Cl{\cdot}N_2{\cdot}C_6H_2(NO_2)_3$, melts at 184—185°. *Trinitronitrosoparachlorazobenzene*,

$$NO_2{\cdot}C_6H_3Cl{\cdot}N_2{\cdot}C_6H_2(NO_2)_2{\cdot}NO,$$

melts at 180—181°. *Trinitronitrosoazobenzenephenylhydrazine*,

$$NHPh{\cdot}NH{\cdot}C_6H_3(NO_2){\cdot}N_2{\cdot}C_6H_2(NO_2)_2{\cdot}NO,$$

melts at 130—131°. *Trinitronitrosoazobenzeneparachlorophenylhydrazine*, $C_6H_4Cl{\cdot}NH{\cdot}NH{\cdot}C_6H_3(NO_2){\cdot}N_2{\cdot}C_6H_2(NO_2)_2{\cdot}NO$, melts at 145—156° (? 146°). *Trinitronitrosoazobenzeneazoparachlorobenzene*, $C_6H_4Cl{\cdot}N_2{\cdot}C_6H_3(NO_2){\cdot}N_2{\cdot}C_6H_2(NO_2)_2{\cdot}NO$, melts at 98—99°. *Trinitronitrosoazobenzenenitroazoparachlorobenzene*,

$$NO_2{\cdot}C_6H_3Cl{\cdot}N_2{\cdot}C_6H_3(NO_2){\cdot}N_2{\cdot}C_6H_2(NO_2)_2{\cdot}NO,$$

melts at 111—112°. *Tetranitronitrosodisazobenzeneparachlorophenylhydrazine*, $C_6H_4Cl{\cdot}N_2H_2{\cdot}C_6H_3(NO_2){\cdot}N_2{\cdot}C_6H_3(NO_2){\cdot}N_2{\cdot}C_6H_2(NO_2)_2{\cdot}NO$, melts at 238—239°. *α-Dinitrophenylparachlorophenylhydrazine*,

$$C_6H_4Cl{\cdot}N_2H_2{\cdot}C_6H_3(NO_2)_2\ [Cl : (NH) = 4 : 1, \text{ and } (NO_2)_2 = 2 : 4],$$

melts at 146—147°. *Dinitroparachlorazobenzene*,

$$C_6H_4Cl{\cdot}N_2{\cdot}C_6H_3(NO_2)_2,$$

melts at 151—152°. *Nitronitrosoparachlorazobenzene*,

$$C_6H_4Cl{\cdot}N_2{\cdot}C_6H_3(NO_2){\cdot}NO,$$

melts at 141—142°. *Dinitrosoparachlorazobenzene*,

$$C_6H_4Cl{\cdot}N_2{\cdot}C_6H_3(NO)_2,$$

melts at 135—136°.

Picrylmetachlorophenylhydrazine forms orange prisms which melt at 178—179° (uncorr.). Two bromo-derivatives of the picrylorthohydrazine compound have been obtained; the lower one crystallises in yellow needles melting at 269°; the higher one in red-yellow needles melting at 170°. A. G. B.

Azoxyphenol Ethers. By L. GATTERMANN and A. RITSCHKE (*Ber.*, **23**, 1738—1750).—In many reactions the phenol ethers behave in a similar manner to the hydrocarbons, and the authors have therefore examined the reduction-products of their nitro-compounds in order to ascertain whether isomerides exist similar to those described by Janovsky for azoxytoluene. In the meantime, however, Hantsch and Werner have shown that in the latter case no isomerism exists, and the authors also find that with the azoxyphenol ethers no isomerism of the ordinary kind exists. As already mentioned, however (see preceding abstract), one of these compounds, namely, parazoxyanisoïl, exists in a yellow and white modification.

Paranitrophenetoïl gave, on reduction with sodium in methyl alcohol solution, a mixture of two compounds, of which the one occurring in larger quantity, is azoxyanisoïl, $O{<}\begin{matrix}N{\cdot}C_6H_4{\cdot}OMe\\ |\\ N{\cdot}C_6H_4{\cdot}OMe\end{matrix}$, and not, as expected, azoxyphenetoïl, $O{<}\begin{matrix}N{\cdot}C_6H_4{\cdot}OEt\\ |\\ N{\cdot}C_6H_4{\cdot}OEt\end{matrix}$. In presence of an excess

of methyl alcohol, the ethyl-group is therefore displaced by methyl. This compound is also obtained by the reduction of paranitranisoïl with sodium in methyl alcohol solution, but if ethyl alcohol is employed, the chief product is azoxyphenetoïl. A subsidiary product is also obtained in this case, identical with the second of the two compounds obtained from paranitrophenetoïl; it has the constitution $O<\begin{matrix}N\cdot C_6H_4\cdot OMe\\ |\\ N\cdot C_6H_4\cdot OEt\end{matrix}$.

An attempt was made to prepare this in larger quantity by reducing a mixture of paranitroanisoïl and paranitrophenetoïl in molecular proportion, with sodium and methyl alcohol. It was found, however, that the paranitrophenetoïl is first completely converted into paranitroanisoïl, which is then reduced to azoxyanisoïl. The same mixture was then reduced with sodium and a mixture of methyl and ethyl alcohols, when a compound was obtained having a different melting point from the mixed compound above described; it is at present being further investigated.

All these compounds when first melted form a milky liquid, which only becomes clear on raising the temperature. Thus azoxyanisoïl melts at 116°, and becomes clear at 134°; azoxyphenetoïl melts at 134°, and becomes clear at 165°; whilst the mixed compound melts at 86°, and becomes transparent at 116°. They belong, therefore, to the class described by Lehmann as fluid crystals. H. G. C.

Phenylsuccinazone. By G. Ciamician and C. U. Zanetti (*Ber.*, **23**, 1784—1787).—A dilute aqueous solution of succinaldioxime, prepared from pyrroline (compare Abstr., 1889, 1208), was gently warmed with five times the quantity of phenylhydrazine acetate; the solution was cooled, and the precipitated phenylsuccinazone purified by recrystallising it once from boiling alcohol; it melted at 124—125°. When it is rubbed in a mortar with 25 times its weight of strong hydrochloric acid, phenylhydrazine hydrochloride separates, and a yellow solution is obtained containing a weak base, which is precipitated in white or pinkish flakes when the solution is diluted with water. It was boiled repeatedly with alcohol and recrystallised from ethyl acetate, forming thin, white needles which melt with decomposition at 184—185°. It dissolves in strong acids, but is precipitated when the solutions are diluted; with sulphuric acid and potassium chromate, it gives a deep blue colour; it yields a yellow, amorphous platinochloride, and it disssolves in ether, boiling ethyl acetate, hot benzene, and acetic acid, sparingly in alcohol, and not at all in light petroleum. An analysis and a molecular weight determination by Raoult's method showed that it has the formula $C_{20}H_{20}N_4$. It appears to be neither a pyrroline- nor a pyridazine-derivative, but is probably closely allied to, perhaps a lower homologue of, the compound $C_{22}H_{24}N_4$, obtained by Ach (this vol., p. 70), by reducing methylphenylpyridazone, $<\begin{matrix}CMe:N\cdot NPh\\ CH:CH\cdot CO\end{matrix}>$ with sodium and alcohol. C. F. B.

Cyanogen Additive Products of some Amidoximes. By O. Nordenskjöld (*Ber.*, **23**, 1462—1464).—*Dicyanobenzenylamidoxime*,

$C_9H_8N_4O$, is precipitated in needles when cyanogen is passed into an alcoholic benzene solution of benzenylamidoxime. It melts at 116°, is only sparingly soluble in benzene, and is gradually decomposed by boiling alcohol and boiling water; it is decomposed by dilute hydrochloric acid and warm soda, and when warmed with acetic anhydride it yields acetylbenzenylamidoxime (m. p. 96°).

Dicyano-β-naphthenylamidoxime, $C_{13}H_{10}N_4O$, separates in crystals when cyanogen is passed into an alcoholic solution of β-naphthenylamidoxime; it melts at 118—119°, and resembles the preceding compound, than which, however, it is rather more readily soluble in benzene. F. S. K.

Isomerism of the Aldoximes. By E. BECKMANN (*Ber.*, 23, 1680—1692).—The author's previous researches on the two isomeric benzaldoximes (Abstr., 1889, 607, 979) have led to the conclusion that their constitution is represented by the formulæ CHPh:N·OH and $\begin{matrix} NH- \\ | \\ CHPh \end{matrix}\!\!>\!O$, the chief ground for this supposition being that their benzyl ethers, in the preparation of which only small quantities of bye-prodncts are formed, contain the benzyl-group attached to the oxygen-atom and to the carbon-atom respectively. Goldschmidt, on the contrary, regards the two oximes as structurally identical, inasmuch as both combine with phenyl cyanate in the absence of water (this vol., p. 253), and his conclusions have been further adopted by Hantzsch and Werner (this vol., p. 318). The author has investigated this reaction more closely, and finds that with the reagent in question intramolecular change readily takes place, even at a low temperature, and that, further, the β-benzyl ether itself can combine with a molecule of phenyl cyanate. Hence, no conclusion as to the presence or absence of a hydroxyl-group can be drawn from the behaviour of this reagent. As regards the formation of benzonitrile from β-benzaldoxime, from which certain theoretical conclusions have been drawn by Hantzsch and Werner (*loc. cit.*), the author shows that this is not formed directly, but that the first product of the reaction is benzamide.

For the preparation of α-benzaldoxime, benzaldehyde is mixed with an excess of 20—25 per cent. soda solution, and hydroxylamine hydrochloride added in small portions at a time; the solution is then extracted with ether, and the oxime precipitated by passing in carbonic anhydride. For further purification, the oxime is added to an alcoholic solution of sodium ethoxide, when the α-sodium salt is precipitated, whilst the β-compound present remains in solution.

β-Benzaldoxime is most readily obtained by passing dry hydrogen chloride into an ethereal solution of the α-compound; the precipitated hydrochloride is washed with ether, and passed into a separating funnel containing ether and a concentrated soda solution. After shaking, the oxime remains in the ether, and is obtained on evaporating the latter in almost the theoretical quantity. It crystallises in rhombic tablets ($a : b : c = 0.5612 : 1 : 0.404$), and if washed with or crystallised from benzene does not undergo spontaneous conversion into the α-oxime.

α-Anisaldoxime is always formed by the direct action of hydroxylamine on anisaldehyde. It is thus obtained in vitreous, rhomboidal crystals which melt at 61—62°, and are soluble in alcohol and still more readily in benzene. Its *benzyl ether*, $C_{15}H_{15}NO_2$, may be obtained from it by the action of sodium ethoxide and benzyl chloride, or by the action of α-benzylhydroxylamine on anisaldehyde. It forms small plates which melt at 46·5°, and does not yield a hydrochloride.

β-Anisaldoxime is prepared from the α-compound in a manner similar to β-benzaldoxime. It is very sparingly soluble in benzene, and may thus be readily separated from the α-compound. It crystallises in slender needles melting at 130—130·5°, and is much more stable towards alcohol than the corresponding β-benzaldoxime, but not towards ether. Its *benzyl ether*, formed from it by the action of sodium ethoxide and benzyl chloride, or obtained directly from anisaldehyde and β-benzylhydroxylamine, crystallises in square, colourless tables melting at 106—107°. Its *hydrochloride* melts at 167—168° with evolution of gas.

By the action of a solution of hydrogen chloride in acetic acid containing acetic anhydride on α-benzaldoxime, the latter is at once converted into the β-compound, and after remaining for two days at the ordinary temperature, large quantities of benzamide separate. If no anhydride is employed, benzamide can only be detected after four days, but in this case no benzonitrile is formed. With anisaldoxime, the same reactions occur, but the formation of the nitrile takes place more readily. For anisamide, the author finds the melting point 163—164°, instead of 137—138°, as given by Henry (*Ber.*, **2**, 666), and has confirmed this by preparing the compound direct from anisic acid.

The above results show that both β-compounds form an intermediate product between the α-oximes and the amide; this is in full agreement with the constitutional formulæ given above.

H. G. C.

A Dimolecular Isomeride of Benzaldoxime. By R. BEHREND and E. KÖNIG (*Ber.*, **23**, 1773—1779).—To an acetic acid solution of β-benzylhydroxylamine, ether was added, and then a solution of potassium dichromate. Some benzaldoxime was formed, and, in addition, a white, crystalline substance separated, and was collected, washed with water, alcohol, and ether, and recrystallised from hot acetic acid or from chloroform. It forms prisms or tables melting at about 127—128°, and is an isomeride of benzaldoxime. It is not, however, isobenzaldoxime, for although it has the same melting point as the latter, it differs in crystalline form, in solubility, in resisting the action of acids, and in being insoluble in alkalis. It dissolves easily in chloroform, sparingly in alcohol, ether, benzene, and acetic acid, and not at all in water. By Raoult's method it was shown to have double the molecular weight of benzaldoxime, and it yields very distinctly Liebermann's reaction for the nitroso-group; hence it is probably a *di-nitrosotoluene*, $(CH_2Ph)_2N_2O_2$, perhaps $\begin{array}{l}CH_2Ph\cdot N\cdot O\\ \quad\quad\;\; | \\ CH_2Ph\cdot N\cdot O\end{array}\!\!>$. When boiled with alcohol, it is transformed quanti-

tatively into isobenzaldoxime. When treated with sodium ethoxide and benzyl chloride, it yields *benzyl-isobenzaldoxime*, $O<\begin{matrix}N\cdot CH_2Ph\\ | \\ CHPh\end{matrix}$, melting at 81—82°; some benzylbenzaldoxime being probably formed at the same time. When warmed with phenol and sulphuric acid, it gives an intense reddish-violet solution; if potash is now added, the colour becomes greenish-yellow to blue-green, and further changes to a pure deep blue on the addition of water. It does not form salts.

The rest of the paper is devoted to a reply to Willgerodt, who has reproached Behrend with not mentioning, in his paper on the stereochemistry of nitrogenous compounds, his (Willgerodt's) work on hydrazines. C. F. B.

Mercurobenzamide. By H. SCHIFF (*Ber.*, 23, 1816—1817; compare Tafel and Enoch, this vol., p. 973).—Mercurobenzamide may be recrystallised from aqueous potash; it is not acted on by either potassium iodide or ethyl bromide. A neutral aqueous solution of mercurobenzamide may be boiled with copper turnings without decomposition taking place. No reaction occurs on boiling ethyl chlorocarbonate with mercurobenzamide suspended in anhydrous ether; if absolute alcohol is used in place of the ether, ethyl carbonate, mercuric chloride, and benzamide are formed. Mercurobenzamide is readily decomposed by acids, or by hydrogen sulphide. Ethyl chlorocarbonate has no action on benzamide suspended in ether, but on boiling with 95 per cent. alcohol, ethyl benzoate and ammonium chloride are obtained. J. B. T.

Derivatives of Amidocinnamic Acid. By F. W. ROTHSCHILD (*Chem. Centr.*, 1890, i, 905—906; *Inaug. Diss., Berlin*).—Orthoamidocinnamic acid is converted into the corresponding carbamide or *orthouramidocinnamic acid*, $NH_2\cdot CO\cdot NH\cdot C_6H_4\cdot C_2H_2\cdot COOH$, by treatment with potassium cyanate in hydrochloric acid solution. If treated with potassium thiocyanate, *thiocyanamidocinnamic acid*,

$$CNS\cdot NH_3\cdot C_6H_4\cdot C_2H_2\cdot COOH,$$

is formed, melting at 152°. When heated at 110—120°, it is converted into *orthothiouramidocinnamic acid*,

$$NH_2\cdot CS\cdot NH\cdot C_6H_4\cdot C_2H_2\cdot COOH,$$

melting at 236—239°. When heated at 100° in a sealed tube with allyl isocyanate, *orthoallylthiouramidocinnamic acid*,

$$C_3H_5\cdot NH\cdot CS\cdot NH\cdot C_6H_4\cdot C_2H_2\cdot COOH,$$

is formed, melting at 204—208°; in like manner, with phenyl isocyanate, it yields *orthophenylthiouramidocinnamic acid*,

$$NHPh\cdot CS\cdot NH\cdot C_6H_4\cdot C_2H_2\cdot COOH,$$

melting point 235—237°. With carbon bisulphide, *orthocarboxycinnamyldithiocarbamic acid*, $CSSH\cdot NH\cdot C_6H_4\cdot C_2H_2\cdot COOH$, is formed, melting at 185—187°.

With meta- and para-amidocinnamic acids, only the thiocyano-derivatives could be obtained. *Metathiocyanamidocinnamic acid*, obtained by means of cuprous thiocyanate, melts at 148—149°. The para-acid does not melt at 272°.

If it is heated rapidly, it suffers decomposition. The corresponding carbamide was obtained. J. W. L.

Oxanilic Acid. By O. ASCHAN (*Ber.*, **23**, 1820—1825).—Oxanilic acid is best prepared by heating 20 grams of aniline with 25 grams of anhydrous oxalic acid, in an oil-bath, at 130—140° for about an hour. The finely divided product is boiled with 300—400 c.c. water, and filtered hot; the aniline oxanilate, which crystallises out on cooling, is well washed with cold water, and decomposed with boiling dilute sulphuric acid—25 c.c. concentrated acid, 475 c.c. water, and 50 grams oxanilate. When cold, the solution is shaken with ether, the ether evaporated, and the residual oxanilic acid purified by recrystallising from water; the yield is 73 per cent. of the aniline employed, as against 15—20 per cent. obtained by the usual method. The salts of oxanilic acid are all sparingly soluble in water, and are very stable towards dilute acids. The *silver*, *lead*, and *mercuric* salts form crystalline precipitates. Hydrogen salts of the alkali metals are prepared by adding a 5 per cent. solution of oxanilic acid to a concentrated solution of an alkaline nitrate. *Hydrogen potassium oxanilate*, $C_{16}H_{13}N_2O_6K + H_2O$, crystallises in long, flat prisms; the corresponding *ammonium salt* forms transparent prisms. *Hydrogen sodium oxanilate*, $C_{16}H_{13}N_2O_6Na + 3H_2O$, is deposited in lustrous leaves, which are very sparingly soluble. *Oxanilyl chloride*, NHPh·CO·COCl, is prepared by the action of phosphorus pentachloride on oxanilic acid; it is deposited from light petroleum in large, lustrous leaves, or flat prisms, melting at 82·5°; it is very hygroscopic. Oxanilide is formed by the action of aniline on oxanilyl chloride, whilst with alcoholic ammonia phenyloxamide is obtained. On adding a large excess of water to oxanilyl chloride, oxanilic acid is immediately formed; if the chloride is treated with half its weight of water, it is decomposed into oxanilide, hydrochloric acid, carbon monoxide, and carbonic anhydride. Phenylcarbamide is obtained by the distillation of the chloride; the yield is 75 per cent. of the theory. J. B. T.

Toluyleneurethane and Tolueneoxamethane. BY H. SCHIFF and A. VANNI (*Ber.*, **23**, 1817—1819).—Toluylenediurethane is best prepared by gradually adding ethyl chlorocarbonate to a well cooled solution of diamidotoluene, dissolved in dilute alcohol; the diurethane immediately separates in crystals melting at 137°. The mother liquor contains diamidotoluene hydrochloride, and toluenesemiurethane hydrochloride. Toluylenediurethane is scarcely affected by heating with alcoholic ammonia at 130—140°. No reaction takes place with aniline in dilute alcoholic solution, but on heating the diurethane with aniline alone, diphenylcarbamide is formed. On heating the diurethane with phenylthiocarbamide, no change occurs; the addition of dilute alcohol causes a complicated decomposition, the chief product being phenylthiourethane, NHPh·CS·OEt. *Toluylenesemi-*

urethane, $NH_2·C_7H_6·NH·COOEt$, is obtained from the mother liquors (see above) by evaporating to dryness, treating with excess of potassium hydroxide, and recrystallising several times from dilute alcohol, in which it is readily soluble; it forms colourless, flat, interlaced needles melting at 90—91°. The *hydrochloride* is readily soluble in water; the *platinochloride* forms small crystals. *Thiocarbanilotoluyleneurethane*, $COOEt·NH·C_7H_6·NH·CS·NHPh$, is obtained, together with diphenylthiocarbamide, by heating toluylenesemiurethane with phenylthiocarbamide and dilute alcohol; it is very sparingly soluble in alcohol, from which it crystallises in colourless prisms melting at 154—155°. *Amidotoluyloxamic acid*,

$$NH_2·C_7H_6·NH·CO·COOH,$$

is formed by boiling toluyldioxamethane, obtained in the preparation of toluyleneoxamethane, with 90 per cent. alcohol for some time; it forms small, hard crystals melting at 222—224°, and is very sparingly soluble in alcohol.

Thiocarbanilotoluyleneoxamethane,

$$NHPh·CS·NH·C_7H_6·NH·CO·COOEt,$$

is obtained by warming phenylthiocarbamide with toluyleneoxamethane dissolved in dilute alcohol. The compound is purified by repeated recrystallisation from alcohol; it forms small, yellowish crystals melting at 154—155°. Two compounds containing sulphur may be separated from the mother liquor: the one is obtained as a yellow, crystalline powder melting at 198°, it is sparingly soluble in warm alcohol, and has the formula $C_7H_6<\genfrac{}{}{0pt}{}{NH·C_2O_2}{NH\ ·\ CS}>NPh$; it is probably formed from the above oxamethane-derivative by elimination of alcohol. The second compound crystallises in lustrous leaves melting at 136—138°, and is only formed in very small quantity.

J. B. T.

Triphenylguanylthiocarbamide and Dicyanodiamide. By B. RATHKE and R. OPPENHEIM (*Ber.*, **23**, 1668—1675; compare Rathke, Abstr., 1887, 662).—Dicyanodiamide is formed from guanylthiocarbamide by elimination of the elements of hydrogen sulphide; in a similar manner, *triphenyldicarbimide* is obtained from triphenylguanylthiocarbamide.

Dicyanodiamide may be represented by one or other of the formulæ $NH_2·CNH·NH·CN$; $NH:C<\genfrac{}{}{0pt}{}{NH}{NH}>C:NH$. The constitution of the triphenyl-derivative can, however, only be expressed by a ring formula, corresponding with the second of the above; as it differs widely in general properties from dicyanodiamide, the latter would appear to be best represented by the open-chain formula. *Triphenyldicarbimide*, $C_{20}H_{16}N_4$, is obtained by boiling an alcoholic solution of triphenylguanylthiocarbamide,

$$NHPh·CS·NH·C(NPh)·NHPh,$$

with freshly precipitated mercuric oxide; it is most conveniently purified by treating the alcoholic solution with hydrochloric acid, and diluting with water; the crystals of the hydrochloride which

separate are then treated with sodium carbonate. The *free base* crystallises with 1 mol. of alcohol, in fine, long, yellowish needles melting at 70—74°. The hydrochloride is very sparingly soluble; it crystallises in slender needles. The platinochloride forms reddish-yellow crystals, containing 1 mol. of water. The sulphate is sparingly soluble. The picrate melts at 53°. The free base may also be prepared by heating diphenylguanidine for an hour at 170—180°; the product is dissolved in alcohol, allowed to stand for 24 hours, filtered, and hydrochloric acid added to the hot solution; the hydrochloride, which separates on cooling, is then treated as above.

Triphenylbiguanide, $C_{20}H_{19}N_5$, is obtained by boiling triphenylguanylthiocarbamide with silver nitrate and ammonia in excess. The silver sulphide is removed, the solution concentrated, and treated with hydrochloric acid; the mixed crystals are separated by recrystallisation from dilute alcohol, in which triphenylbiguanide hydrochloride is readily soluble. The free *base* crystallises from alcohol in colourless prisms melting at 137°. The hydrochloride crystallises from alcohol in thin, pointed prisms. The platinochloride forms reddish-yellow crystals. The nitrate, oxalate, and acetate have also been prepared. The same base may be obtained by treating diphenylguanidine with phenylcyanamide in ethereal solution; after remaining for a week, the ether is evaporated, and the residue treated first with hydrochloric acid, and then with ether; the insoluble portion consists of triphenylbiguanide hydrochloride.

Triphenylthiammeline has already been prepared; it is also formed by boiling the additive compound of diphenplguanidine and phenylthiocarbamide with alcohol and mercuric thiocyanide.

Experiments have shown that ammonia, or thiocyanic acid, only reacts with triphenyldicarbimide at the moment of its formation.

J. B. T.

Action of Hydroxylamine and its Derivatives on the Thiocarbimides. By L. VOLTMER (*Chem. Centr.*, 1890, i, 861—862; from *Inaug. Diss.*, *Berlin*).—Hydroxylamine and phenylthiocarbimide combine together at ordinary temperatures with formation of *phenylhydroxythiocarbamide*, NHPh·CS·NH·OH, which decomposes, when melted, into a gas and an oily product. The alcoholic solution, which is slightly acid, is coloured violet by very dilute ferric chloride. By heating the alcoholic solution, sulphur and phenylcyanamide are formed; the latter melts at 39—40°. If hydroxylamine and the thiocarbimide are heated together, the same reaction seems to occur. Ethoxylamine reacts similarly with phenylthiocarbimide with formation of *phenylethoxythiocarbamide*,

NHPh·CS·NH·OEt,

which melts at 103° without decomposition. It is more stable than the first named; but by boiling its solution sulphur, alcohol, and phenylcyanamide are formed.

Phenylmethoxythiocarbamide melts at 115°. *Phenylbenzyloxythiocarbamide*, NHPh·CS·NH·OC_7H_7, prepared from benzylhydroxylamine and phenylthiocarbimide, melts at 105°. *Orthotolylhydroxythiocarbamide* is obtained at ordinary temperature from the action of

orthotolylthiocarbimide in chloroform on hydroxylamine; it melts at 92°. *Orthotolylcyanamide*, obtained from this by warming the solution, melts at 77°. When heated with hydrochloric acid, it is converted into monotolylcarbamide. *Orthotolylbenzyloxythiocarbamide* melts at 125°; *α-naphthylhydroxythiocarbamide*, $C_{10}H_7 \cdot NH \cdot CS \cdot NH \cdot OH$, prepared from the thiocarbimide and hydroxylamine, melts at 116°. Ferric chloride colours the alcoholic solution from dark-yellow to green. The α-naphthylcyanamide obtained from it melts at 150°. The corresponding benzyloxycarbamide melts at 132—133°.

Allylthiocarbimide reacts violently with hydroxylamine with separation of sulphur, but the corresponding carbamide could not be obtained.

Carbanil and benzylhydroxylamine react together with formation of *phenylbenzyloxycarbamide*, $NHPh \cdot CO \cdot NH \cdot OC_7H_7$, melting at 106°. It is very stable. J. W. L.

Paramethoxydihydroxydihydroquinoline and a New Case of Stereochemical Isomerism. By A. EICHENGRÜN and A. EINHORN (*Ber.*, 23, 1489—1494).—*Orthonitrometachlorophenylbromopropionic acid*, prepared by treating orthonitrometachlorocinnamic acid with hydrobromic acid, crystallises from alcohol in needles melting at 142·5—143·5°; when carefully neutralised with concentrated ammonia in the cold, it yields a lactone which crystallises from ethyl acetate in prisms melting at 147°, and shows all the properties of an orthonitro-β-lactone. When this lactone is boiled with alkalis, it is converted into orthonitrometachlorophenyllactic acid; this acid can also be obtained from orthonitrometachlorophenylbromopropionic acid by dissolving it in warm ammonia and heating the resulting *orthonitrometachlorophenyllactamide*, a crystalline substance melting at 148°, with dilute sulphuric acid.

Orthonitrometachlorophenyllactic acid separates from water and ether in crystals and melts at 152°; when heated under pressure with potassium methoxide and methyl alcohol, it is converted into the sparingly soluble potassium salt of orthonitrometamethoxyphenyllactic acid, from which the free acid can be obtained by decomposition with a dilute mineral acid.

Orthonitrometamethoxyphenyllactic acid crystallises from water in colourless plates melting at 106°; on reduction with ferrous sulphate and ammonia, it yields *paramethoxydihydroxydihydroquinoline*, $OMe \cdot C_6H_4 <\begin{matrix} CH(OH) \\ N:C(OH) \end{matrix}> CH_2$, and small quantities of paramethoxycarbostyril. Orthonitrometamethoxyphenyllactic acid can also be obtained by warming orthonitrometachlorocinnamic acid with potassium methoxide in methyl alcoholic solution; the *orthonitrometamethoxycinnamic acid* thus produced crystallises from alcohol in long needles, melts at 225°, and combines with hydrogen bromide, yielding *orthonitrometamethoxyphenyl-β-bromopropionic acid*, which crystallises from a mixture of chloroform and light petroleum in needles melting at 162—163°. When this bromo-acid is carefully neutralised with sodium carbonate or alcoholic ammonia in the cold, it is converted into a lactone, which separates from ethyl acetate in prisms

melting at 124—125°; but when it is treated with warm ammonia, it dissolves, yielding a reddish solution, from which *orthonitrometamethoxyphenyllactamide* is deposited after some time in small, colourless plates melting at 187—188°. The last-named compound can be converted into orthonitrometamethoxyphenyllactic acid by boiling it with dilute sulphuric acid.

Orthonitrometachlorophenyl-β-lactic acid methyl ketone is obtained, together with the ketones of orthonitrometachlorophenyl-β-lactic acid and orthonitrometachlorocinnamic acid, by the condensation of orthonitrometachlorobenzaldehyde with acetone; it crystallises from alcohol in plates, melts at 106·5—107·5°, and, when heated at 70—80° with a solution of sodium hypochlorite, it is converted into orthonitrometachlorophenyl-β-lactic acid with liberation of chloroform. This acid, the constitution of which is proved by its method of formation, crystallises from dilute alcohol in colourless, hexagonal plates, melts at 156°, and has properties entirely different from those of the orthonitrometachlorophenyllactic acid (m. p. 152°) obtained from orthonitrochlorocinnamic acid as described above. Experiments have shown that the two compounds are stereochemically isomeric, but attempts to convert the one into the other by heating with water, alcohol, or dilute mineral acids under pressure were unsuccessful, the acid prepared from cinnamic acid remaining unchanged under those conditions, that prepared from the ketone being decomposed into cinnamene-like compounds. The isomerism of the two compounds is proved by the following experiments:—When the thick, oily orthonitrometachlorophenyllactic aldehyde, obtained by the condensation of orthonitrometachlorobenzaldehyde with acetaldehyde in presence of 6 per cent. soda, is oxidised with freshly precipitated silver oxide in alcoholic solution, considerable quantities of the more stable acid (m. p. 152°) are obtained; but if the aldehyde is oxidised by warming it with a solution of sodium hypochlorite, the labile acid is formed.

As, therefore, either acid can be obtained at will from one and the same aldehyde simply by varying the oxidising agent, there can be no doubt that they are stereochemically isomeric, the isomerism being due to the presence of an asymmetric carbon-atom. Molecular weight determinations by Raoult's method proved that the two compounds are not polymeric.

Attempts to displace the chlorine-atom by the methoxy-group in the acid (m. p. 156°) prepared from the ketone have hitherto been unsuccessful, and no pure compound has yet been obtained from it by reduction with ferrous sulphate and ammonia; the isomeride, on the other hand, is easily converted into a *chlorodihydroxydihydroquinoline*, melting at 172°. F. S. K.

Phenetoïlphthaloylic Acid. By E. Grande (*Chem. Centr.*, 1890, i, 822; from *Ann. Chim. Farm.* [4], **10**).—By means of Friedel and Craft's reaction with aluminium chloride on phthalic anhydride and phenetoïl, *phenetoïlphthaloylic acid*, $COOH\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot OEt$, is obtained. It melts at 135—136°, also in boiling water; it is sparingly soluble in boiling water, but readily in hot alcohol, ether, benzene, carbon bisulphide, and hot toluene. The neutral solution of the ammo-

nium salt gives the following reactions:—With mercuric chloride, a white, crystalline precipitate; with cupric sulphate, a pale-blue, crystalline precipitate; with ferric chloride, a yellow, crystalline precipitate; and with plumbic acetate, a white, crystalline precipitate. The potassium and calcium salts are readily soluble in water and alcohol; the barium salt crystallises with 5 mols. H_2O, is soluble in water and alcohol, and has a sweet taste; the silver salt is sparingly soluble in water, and is stable in daylight. J. W. L.

β- and δ-Benzallevulinic Acid. By H. ERDMANN (*Annalen*, **258**, 129—133).—The method described by Erlenmeyer (Abstr., 1890, 495) for the preparation of β-benzallevulinic acid does not yield this compound, but an isomeride which has the constitution $CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, and is, therefore, a δ-benzallevulinic acid. This compound melts at 120°, and differs from the β-acid (Abstr., 1890, 375) both in chemical and physical properties; its behaviour with bromine is different from that of the β-acid; it is converted into a neutral compound by acetic anhydride in the cold, and nascent hydrogen transforms it into a δ-benzyllevulinic acid which melts at 87—88°. The δ-benzallevulinic acid combines with hydroxylamine, yielding an *oxime*, $C_{12}H_{13}O_3N$, which crystallises in yellowish prisms, melts at 148—149°, and has a strongly acid reaction; its salts are also totally different from those of the β-acid.

Metachlorobenzaldehyde and levulinic acid condense together in alkaline solution, yielding *metachloro-δ-benzallevulinic acid*, $C_{12}H_{11}ClO_3$, which melts at 128°. β-Benzallevulinic acid and benzaldehyde under the same conditions give *βδ-dibenzallevulinic acid*,

$$CHPh{:}CH{\cdot}CO{\cdot}C(CHPh){\cdot}CH_2{\cdot}COOH$$

(m. p. 146°). Both β- and δ-benzallevulinic acids can be obtained by the condensation of their components in acid solution. The investigation of the δ-acid is being continued. F. S. K.

Synthesis of Homopiperic and Piperic Acids. By S. GABRIEL (*Ber.*, **23**, 1767—1773).—1·1 gram of sodium is dissolved in 10 c.c. of absolute alcohol, 15 grams of ethyl malonate, and then 10 grams of bromopropylphthalimide added, the mixture boiled for an hour in a reflux apparatus, and the alcohol and unchanged ethyl malonate driven over with steam. The residue is repeatedly extracted with light petroleum, and the solution on cooling deposits *ethyl γ-phthalimidopropylmalonate*, $C_6H_4{<}{CO \atop CO}{>}N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOEt)_2$, in brilliant, colourless, monoclinic crystals, which melt at 46—48°, and dissolve readily in most solvents, sparingly in light petroleum, and not at all in water. When it is heated with hydrochloric acid (sp. gr. 1·13) for 3 hours at 180—190° in a sealed tube, it is decomposed, yielding phthalic acid, carbonic anhydride, ethyl chloride, and δ-amidovaleric (homopiperic) acid, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, which was shown to be identical with that obtained by Schotten from benzoylpiperidine.

Chlorobutyronitrile was prepared by treating trimethylene chloro-

bromide with potassium cyanide. It was then heated with an equivalent quantity of potassiophthalimide at 150—180°, and the γ-cyanopropylphthalimide formed was heated with dilute sulphuric acid; γ-amidobutyric acid was thus obtained, and found to be identical in its properties with the piperic acid prepared by Schotten's method from piperylurethane.

Schotten had previously shown that neither δ-amidovaleric nor γ-amidobutyric acid is poisonous, whilst the anhydride of the former (piperidone or oxypiperidine) is so. He has lately shown, at the request of the author, that pyrrolidone, the anhydride of γ-amidobutyric acid, is a poison of the same nature as piperidone, acting upon the nervous system, and causing death by tetanic convulsions when administered in sufficiently large quantity. C. F. B.

Oxidation of Gallic Acid, Tannin, and Oak Tannins. By C. BOETTINGER (*Annalen*, **257**, 248—252).—When oak-bark-red or oak-red is treated with cold very dilute nitric acid, carbonic anhydride is evolved, and after some time the reaction becomes so energetic that the mixture must be cooled with water. If the solution thus obtained is evaporated, rapid oxidation ensues, and there remains a mixture of oxalic acid and various other acids, which can be separated by means of their calcium salts. The quantity of the calcium salts (excluding calcium oxalate) thus obtained is only about 6 per cent. of the material employed.

The acetyl-derivative of oak-wood tannin gives identical oxidation-products. Tannin and gallic acid, on oxidation with nitric acid, also yield compounds other than oxalic acid and carbonic anhydride. After removing the oxalic acid as completely as possible and treating the residue with calcium carbonate, a readily soluble and a very sparingly soluble calcium salt are obtained. The latter contains 16·39 per cent. of calcium, and seems to be calcium trihydroxyglutarate ($+ H_2O$); the latter contains 12·4 per cent. of calcium, and is probably calcium trihydroxybutyrate. A calcium salt, which seems to be that of trihydroxybutyric acid, was also isolated from the oxidation-products of oak-bark-red, oak-red, and the acetyl-derivative of oak-bark tannin. F. S. K.

Reduction-products of Terephthalic Acid. By A. BAEYER and J. HERB (*Annalen*, **258**, 1—49).—The authors have prepared and investigated a number of new derivatives of the hydroterephthalic acids (compare Baeyer, Abstr., 1889, 1176); their experiments have shown that the $\Delta^{1:4}$ and $\Delta^{2:5}$ dihydro- acids can be converted into tetrabromides, but that the $\Delta^{1:3}$ and $\Delta^{1:5}$ dihydro- acids can only combine with two bromine atoms. The dibromides of the four dihydroterephthalic acids ($\Delta^{1:4}$, $\Delta^{2:5}$, $\Delta^{1:3}$, and $\Delta^{1:5}$) are all converted into terephthalic acid by treatment with alcoholic potash; this behaviour on the part of the $\Delta^{1:3}$ and $\Delta^{1:5}$ acid affords additional evidence of the existence of a para-binding in benzene, as may be seen by studying the constitutional formulæ of the dibromides in question.

A cheaper method for the preparation of terephthalic acid than that described by Baeyer (Abstr., 1888, 1072) is to convert paratoluidine

into the nitrite by Sandmeyer's reaction, hydrolyse the product with boiling moderately dilute (3 : 2) sulphuric acid (10 parts), and oxidise the paratoluic acid thus obtained with an alkaline solution of potassium permanganate. The terephthalic acid is separated from small quantities of unchanged paratoluic acid by treating the crude product with phosphoric chloride and methyl alcohol consecutively, recrystallising the methyl salt thus formed from 96 per cent. alcohol, and then hydrolysing the pure compound; the yield of pure acid is 95—98 per cent. of the paratoluidine employed.

Methyl $\Delta^{2:5 \text{ cistrans}}$ *dihydroterephthalic acid dibromide* can be obtained by treating methyl $\Delta^{2:5}$ dihydroterephthalate (8 grams) with bromine (6·5 grams) in chloroform solution; it separates from light petroleum in transparent, monosymmetrical crystals, $a : b : c = 1·5055 : 1 : 1·2218$, $\beta = 66° 37'$, melts at 110°, and is readily soluble in ether, chloroform, light petroleum, and alcohol. When treated with alcoholic potash, or with a mixture of concentrated sulphuric acid, glacial acetic acid, and water, it is converted into terephthalic acid; on reduction with zinc-dust and glacial acetic acid, it is transformed into methyl $\Delta^{2:5}$ dihydroterephthalate, a fact which shows that the two bromine-atoms are in combination with adjacent carbon-atoms. Methyl $\Delta^{2:5 \text{ cis}}$ dihydroterephthalate does not give a solid dibromide.

Methyl $\Delta^{2:5 \text{ cistrans}}$ *dihydroterephthalate tetrabromide*, prepared by treating the methyl salt (10 grams) with bromine (20 grams) in chloroform solution, separates from light petroleum in transparent, monosymmetrical crystals, $a : b : c = 1·3412 : 1 : 0·59061$, $\beta = 82° 3'$, melts at 98°, and is readily soluble in chloroform, ether, alcohol, and light petroleum. When hydrolysed with alcoholic potash, it yields terephthalic acid and bromoterephthalic acid, and on reduction with zinc-dust and glacial acetic acid, it is converted into methyl $\Delta^{2:5}$ dihydroterephthalate (m. p. 77°), a reaction which proves that both pairs of bromine-atoms are combined with adjacent carbon-atoms. It is not changed even on prolonged heating with a mixture of sulphuric acid, glacial acetic acid, and water. Methyl $\Delta^{2:5 \text{ cis}}$ dihydroterephthalate does not give a solid tetrabromide.

When methyl $\Delta^{2:5 \text{ cistrans}}$ dihydroterephthalate is heated at 100° for three days in a stream of carbonic anhydride, it undergoes no change; the fact, observed by Baeyer, that when heated in the air it is converted into methyl terephthalate is, therefore, due to oxidation.

Diphenyl $\Delta^{2:5 \text{ cistrans}}$ *dihydroterephthalate* is obtained when $\Delta^{2:5 \text{ cistrans}}$ dihydroterephthalic acid is converted into the chloride by means of phosphoric chloride, and the product warmed with the calculated quantity of phenol. It separates from alcohol in small crystals, melts at 146°, and is only sparingly soluble in ether, alcohol, and light petroleum. The corresponding salt of the $\Delta^{2:5 \text{ cis}}$ acid is a colourless oil, readily soluble in light petroleum; when the chloride of the $\Delta^{2:5 \text{ cis}}$ dihydro-acid is warmed with phenol, the larger proportion undergoes intramolecular change, and the principal product is phenyl $\Delta^{2:5 \text{ cistrans}}$ dihydroterephthalate (m. p. 146°), small quantities of a phenyl salt melting above 150° being also produced.

$\Delta^{1:5}$ *Dihydroterephthalic acid dibromide* can be obtained by treating the acid chloride with bromine, and then warming the product with

a concentrated solution of formic acid. It separates from glacial acetic acid in the form of a colourless, crystalline powder, and when boiled with soda it is converted into $\Delta^{1:4}$ dihydroterephthalic acid; alcoholic potash transforms it into terephthalic acid, and on reduction with zinc-dust and acetic acid, it is converted into the $\Delta^{1:5}$ dihydro-acid. The tetrabromide could not be obtained.

Barium $\Delta^{1:5}$ *dihydroterephthalate*, $C_8H_6O_4Ba + 4H_2O$ separates from cold water in colourless, rhombic crystals, $a : b : c = 0.3191 : 1 : 0.3520$, and quickly turns red on exposure to the air.

Methyl $\Delta^{1:3}$ *dihydroterephthalate dibromide* can be obtained by brominating the methyl salt of the dihydro-acid in chloroform solution; it crystallises from cold methyl alcohol in thin, colourless, seemingly monoclinic plates, melts at 64°, and is readily soluble in alcohol, ether, and light petroleum. When warmed with alcoholic potash, it is converted into terephthalic acid, and on reduction with zinc-dust and glacial acetic acid, it yields methyl $\Delta^{1:3}$ dihydroterephthalate and methyl Δ^2 tetrahydroterephthalate, the last-named compound being formed by the reduction of the methyl salt of the $\Delta^{1:3}$ dihydro-acid. Attempts to prepare a tetrabromide were unsuccessful.

Diphenyl $\Delta^{1:3}$ *dihydroterephthalate*, prepared by warming the acid chloride with phenol, crystallises from methyl alcohol in needles, melts at 175°, and is only sparingly soluble in alcohol, ether, light petroleum, and chloroform, but more readily in boiling alcohol.

Methyl $\Delta^{1:3}$ *dihydroterephthalate dihydrobromide*, prepared by treating the acid chloride with methyl alcohol, is an oil; when it is dissolved in methyl alcohol and hydrogen chloride passed into the solution, it is converted into the crystalline modification (m. p. 171°), and on reduction with zinc-dust and glacial acetic acid, it yields methyl Δ^2 tetrahydroterephthalate (m. p. 3°); on hydrolysis with alcoholic potash, it gives the $\Delta^{1:3}$ dihydro-acid.

Barium $\Delta^{1:3}$ *dihydroterephthalate*, $C_8H_6O_4Ba + 4H_2O$, separates from cold water in large, colourless crystals which are identical crystallographically with those of barium $\Delta^{1:5}$ dihydroterephthalate, but which, unlike the latter, do not turn reddish on exposure to the air; the identity of crystalline form is not due to an intramolecular change of one acid into the other, because the barium salts, on decomposition with hydrochloric acid, yield the $\Delta^{1:3}$ and $\Delta^{1:5}$ acid respectively.

Methyl $\Delta^{1:4}$ *dihydroterephthalate tetrabromide* was obtained after many unsuccessful experiments by treating the methyl salt with bromine. It forms transparent, monosymmetrical crystals, $a : b : c = 1.2356 : 1 : 0.9170$, $\beta = 81° 54'$, melts at about 149°, and is much more readily soluble in most solvents than the lactone of methyl hydrogen tribromohexahydroterephthalic acid (compare Baeyer, Abstr., 1888, 1073). It undergoes no change when it is warmed for five hours with a mixture of glacial acetic acid, concentrated sulphuric acid and water; since methyl $\Delta^{1:4}$ dihydroterephthalate dibromide under these conditions is converted into the methyl hydrogen salt, the methyl-group must be eliminated from that carboxy-group which is not adjacent to a bromine-atom.

Phenyl $\Delta^{1:4}$ *dihydroterephthalate* separates from methyl alcohol in small scales, melts at 191°, and is very sparingly soluble in boiling

alcohol, but rather more readily in chloroform. The *barium* salt, $C_8H_6O_4Ba + 4H_2O$, is very sparingly soluble in water, and is identical crystallographically with the barium salt of $\Delta^{1:5}$ and of $\Delta^{1:3}$ dihydroterephthalic acid.

Phenyl Δ^1 tetrahydroterephthalate separates from alcohol in monosymmetrical crystals, $a : b : c = 2·8244 : 1 : 2·4702$, $\beta = 82° 33'$, melts at 145°, and is only moderately easily soluble in alcohol, ether, chloroform, and light petroleum, but readily in the warm solvents. The *hydrobromide* of the phenyl salt, prepared from the hydrobromide of the tetrahydro-acid, separates from methyl alcohol in crystals melting at 127° Δ^1 Tetrahydroterephthalic acid hydrobromide forms monosymmetrical crystals, $a : b : c = 0·37093 : 1 : 0·48370$, $\beta = 72° 31'$, and is identical with Δ^2 tetrahydroterephthalic acid hydrobromide.

Barium Δ^1 tetrahydroterephthalate, $C_8H_8O_4 + 3\frac{1}{2}H_2O$, separates from cold water in forms identical crystallographically with those of the barium salt of $\Delta^{1:5}$ and of $\Delta^{1:3}$ dihydroterephthalic acid; when an aqueous solution of the barium salt is evaporated on the water-bath, crystals containing $1\frac{1}{2}$ mols. H_2O are obtained.

Three geometrically isomeric methyl salts of $\Delta^{2\,\mathrm{cistrans}}$ tetrahydroterephthalic acid dibromide are formed when methyl Δ^2 tetrahydroterephthalate (m. p. 3°), prepared by saturating a methyl alcoholic solution of the acid with hydrogen chloride, is treated with excess of bromine in chloroform solution. After evaporating the chloroform, the residue is dissolved in ether, the ethereal solution decolorised with sulphurous acid, washed with sodium carbonate, mixed with an equal volume of light petroleum, and dried over calcium chloride; the semi-solid mass which remains on evaporating the filtered solution is dissolved in a little hot methyl alcohol, and the solution allowed to cool slowly, whereon a compound is deposited in long needles melting at 171°. This same substance can be obtained by brominating methyl Δ^3 tetrahydroterephthalate, prepared from the silver salt and methyl iodide; it is soluble in methyl alcohol, ether, acetone, chloroform, and light petroleum. When the methyl alcoholic mother liquors from the compound melting at 171° are carefully evaporated at a low temperature, a second modification is deposited in large, transparent crystals, $a : b : c = 1·4638 : 1 : 1·9222$, $\beta = 80° 52'$, which melt at 51°; this substance is much more readily soluble than the isomeride melting at 171° and dissolves freely in methyl alcohol, ethyl alcohol, acetone, ethyl acetate, chloroform, light petroleum, &c. The third modification separates in colourless crystals when the freshly prepared crude product is dissolved in acetone (about $1\frac{1}{2}$ vols.), and the solution kept at a low temperature; it melts at 94°, and as regards solubility, it is about intermediate between the two other isomerides. When methyl Δ^2 tetrahydroterephthalate which has been prepared from the acid chloride is treated with bromine, the product is an oil, from which a trace of a crystalline substance melting at about 20° is deposited after some time; owing to its low melting point, this compound could not be isolated, but the oily product, which may be simply a mixture, and the three crystalline modifications described above have the following properties in common: (1.) On reduction with zinc-dust and glacial acetic acid, they are reconverted into methyl Δ^2 tetrahydro-

terephthalate (m. p. 3°), a reaction which shows that in all the modifications the two bromine-atoms are in the ortho-position to one another. (2.) When treated with alcoholic potash, they yield $\Delta^{1:3}$ dihydroterephthalic acid and terephthalic acid.

Phenyl $\Delta^{2\,\mathrm{cistrans}}$ *tetrahydroterephthalate* is obtained, together with a substance which seems to be a mixture of the phenyl salts of terephthalic acid and Δ^1 tetrahydroterephthalic acid, when the Δ^2 tetrahydro-acid is treated with phosphoric chloride, and the acid chloride thus produced is warmed with phenol. It crystallises from a mixture of benzene and light petroleum in plates, melts at 107° (?), and is readily soluble in benzene, ether, and acetone, but only sparingly in light petroleum.

$\Delta^{2\,\mathrm{cistrans}}$ *Tetrahydroterephthalic acid hydriodide*, prepared by treating the acid with hydriodic acid of sp. gr. 1·96 for several days in the cold, and then warming the mixture for a short time, separates from alcohol in colourless plates, and is gradually decomposed by boiling water.

Benzyl $\Delta^{2\,\mathrm{cistrans}}$ *tetrahydroterephthalate*, prepared by warming the silver salt with benzyl chloride, separates from alcohol in crystals, and melts at 48°.

Phenyl $\Delta^{2\,\mathrm{cistrans}}$ *hexahydroterephthalate* crystallises from acetone in large colourless, monoclinic needles, $a : b : c = 0·48619 : 1 : 0·35093$, $\beta = 75° 6'$, and is only sparingly soluble in ether, alcohol, and light petroleum.

Phenyl terephthalate melts at 194°, not at 191°.

When Δ^1 tetrahydroterephthalic acid is oxidised with a 5 per cent. alkaline solution of potassium permanganate, it is converted into oxalic acid and oily acids, the nature of which could not be determined. The Δ^2 tetrahydro-acid, under the same conditions is converted into succinic acid, a crystalline acid melting at about 150°, and an amorphous acid, but when treated with an alkaline solution of potassium ferricyanide, it is simply oxidised to terephthalic acid.

F. S. K.

Benzylmethylsuccinic and Benzyldimethylsuccinic Acids. By C. A. Bischoff and A. v. Kuhlberg (*Ber.*, **23**, 1942—1950).—In the description of benzylmethylsuccinic acid (this vol., p. 774) it was stated that the acid was probably a mixture of two geometrical isomerides. The authors have now succeeded in proving this supposition and in separating the two compounds. The first, or meso-acid is prepared by boiling the anhydride with water, and melts at 138°, whilst the second, or para-acid is formed when the mixture of acids is heated with hydrochloric acid at 200—240°, and forms slender needles melting at 159—160°.

The ethyl salt obtained by the action of benzyl chloride on ethyl sodisobutenyltricarboxylate does not, as was expected, yield, on hydrolysis, a mixture of benzylisobutenyltricarboxylic and benzyldimethylsuccinic acids, but gives a product from which the seven following acids have been isolated: *Isobutenyltricarboxylic acid*, $COOH·CMe_2·CH(COOH)_2$, melting at 147—149°; *asymmetrical dimethylsuccinic acid*, $COOH·CH_2·CMe_2·COOH$, melting at 140°; *dibenzylmalonic acid*, $C(CH_2Ph)_2(COOH_2)$, melting at 171°; *dibenzyl-*

acetic acid, $CH(CH_2Ph)_2 \cdot COOH$, melting at 85—87°; *benzylmethylcarboxyglutaric acid*, $COOH \cdot CHMe \cdot CH_2 \cdot C(CH_2Ph)(COOH)_2$, melting at 178°; *benzylmethylglutaric acid*,

$$COOH \cdot CHMe \cdot CH_2 \cdot CH(CH_2Ph) \cdot COOH,$$

melting at 128—130°; and, lastly, *benzylsuccinic acid*,

$$COOH \cdot CH_2 \cdot CH(CH_2Ph) \cdot COOH,$$

melting at 153—155°. The formation of the first two acids is readily explained by assuming that the sodium compound is partially reconverted into ethyl isobutenyltricarboxylate, of which these are the normal products of hydrolysis. H. G. C.

Anhydrides of the Diphenylsuccinic Acids. By H. TILLMANNS (*Annalen*, **258**, 87—94).—The anhydride of α-diphenylsuccinic acid (m. p. 183°), prepared by treating the acid with acetic chloride, melts at 111—112°, that of the β-acid (m. p. 229°), prepared in like manner, melts at 112°; by treatment with potash, the anhydrides are reconverted into α- and β-diphenylsuccinic acids respectively. The α-acid melts at 183°, but immediately solidifies again, and does not become permanently liquid until the temperature has risen to 220—222°; if the acid is kept at 220—222° for some time, and then crystallised from chloroform, the anhydride (m. p. 111—112°) is obtained, but if it is simply heated to about 185° for a short time, and then treated with chloroform, the anhydride (m. p. 111—112°) passes into solution whilst β-diphenylsuccinic acid (m. p. 229°) remains undissolved. When the β-acid is heated above its melting point, it is gradually converted into the anhydride of the α-acid. F. S. K.

Phenylmalic Acids. By H. ALEXANDER (*Annalen*, **258**, 67—86). —Ethyl phenylhydroxyacetate crystallises in needles, and melts at 26—27°, not at 75° as stated by Naquet and Longuinine (*Annalen*, **139**, 301). Ethyl phenylbromacetate is a colourless oil boiling at 143—145° (10 mm.) with slight decomposition. Ethyl phenylcarboxysuccinate, $COOEt \cdot CHPh \cdot CH(COOEt)_2$, prepared by treating ethyl sodiomalonate with ethyl phenylbromacetate, as described by Spiegel (*Annalen*, **219**, 31), crystallises from alcohol in colourless needles, melts at 45—46°, and boils at 202°. The free acid crystallises in plates, and melts at 171°, not at 191° as stated by Spiegel. The *silver* salt, $C_{11}H_7Ag_3O_6$, is crystalline and moderately stable. The potassium and the sodium salts are readily soluble in water, but the barium salt is only sparingly soluble. The *calcium* salt, $(C_{11}H_7O_6)_2Ca_3$, is soluble in cold water, but on boiling the solution it is deposited in needles containing 10 mols. H_2O; the crystals lose 2 mols. H_2O over sulphuric acid. *α-Phenylmalic acid* (*α-phenyl-α-hydroxysuccinic acid*),

$$COOH \cdot CH_2 \cdot CPh(OH) \cdot COOH,$$

is obtained, together with phenylmaleic anhydride, by brominating phenylsuccinic acid, according to Volhard's method, and decomposing the unstable bromo-acid thus produced with hot water; the products are extracted with ether and separated by means of chloroform, in

which phenylmaleic acid is only very sparingly soluble. It crystallises from boiling chloroform in very small prisms, melts at 187—188°, and is readily soluble in ether, and moderately easily in water; alcohol converts it into an oil. The lead, iron, and silver salts are insoluble; the salts of the alkalis and alkaline earths dissolve readily in water. When the acid is heated to its melting point, water-vapour and not inconsiderable quantities of carbonic anhydride are evolved, and a crystalline compound melting at 105—106°—probably atropic acid—sublimes in colourless needles; the resinous residue contains small quantities of a crystalline acid melting at 161—162°, possibly phenylfumaric acid.

Phenylmaleic anhydride, $C_{10}H_6O_3$ (see above), crystallises from boiling carbon bisulphide in colourless needles, melts at 119—119·5°, and is readily soluble in chloroform and ether, but only sparingly in carbon bisulphide and light petroleum, and insoluble in water.

Phenylmaleic acid, $C_{10}H_8O_4$, is obtained when the finely-divided anhydride is left for a long time in contact with water, the clear solution extracted with ether, and the extract evaporated at the ordinary temperature. It melts at a temperature below 100°, is moderately easily soluble in cold water, and is very readily converted into the anhydride.

β-Phenylmaleic acid (β-phenyl-α-hydroxysuccinic acid),

$$COOH{\cdot}CH(OH){\cdot}CHPh{\cdot}COOH,$$

can be obtained, together with the oily ethyl hydrogen salt,

$$COOH{\cdot}CH(OH){\cdot}CHPh{\cdot}COOEt,$$

by treating ethyl phenylformylacetate, prepared by Wislicenus' method (Abstr., 1888, 129), with hydrochloric acid and boiling the product for a short time with concentrated hydrochloric acid. It separates from ether in colourless crystals, begins to soften at 150°, and melts completely at 160° with elimination of water, yielding a sublimate of phenylmaleic anhydride (m. p. 119°). It is very readily soluble in water, but only sparingly in hot chloroform, and insoluble in light petroleum and carbon bisulphide. The salts of the alkalis and alkaline earths are readily soluble in water. The barium salt crystallises in flat prisms; the lead and the unstable silver salts are sparingly soluble or insoluble in water. When the acid is boiled with potash, it is converted into a crystalline compound—most probably phenylacetic acid—which melts at 74·5—75°. F. S. K.

Diparatoluylene Sulphoxide. By H. C. Parker (*Ber.*, 23, 1844—1846).—*Diparatoluylene sulphoxide*, $SO(C_6H_4Me)_2$ [Me·SO = 1 : 4], is prepared by heating toluene with thionyl chloride and aluminium chloride; when cold the product is poured into water, and the oil which separates is washed with aqueous soda, and dried; after evaporating the excess of toluene, the residue is recrystallised from light petroleum, from which it is deposited in long, white, flat crystals melting at 92°. The compound is readily soluble in the ordinary menstrua. The corresponding sulphide is obtained by reduction, and the sulphone is formed on oxidation.

In addition to the methods already known, diphenyl sulphoxide may be obtained by the action of thionyl chloride on mercurodiphenyl, or by titrating benzenesulphinic acid with phosphoric anhydride.

J. B. T.

Displacement of the Sodium in Ethyl Sodiophenylsulphone-acetate. By R. OTTO and A. RÖSSING (*Ber.*, 23, 1647—1653).—A reply to the paper of A. Michael (compare this vol., p. 781). The authors give details of further experiments which they have made with the object of deciding this question. They find that dry sodium ethyl phenylsulphoneacetate is entirely unacted on by heating in a sealed tube with ethyl bromide at 125°. If heated in the same manner with ethyl iodide at 150°, methylphenylsulphone is formed. The same result is obtained by heating at 100° a mixture of pure dry ethyl phenylsulphone acetate dissolved in alcohol, sodium ethoxide, and ethyl iodide; one portion was heated in a flask, and a second in a sealed tube. A similar experiment with methyl alcohol and ethyl bromide was also made without success.

The alcohol employed had been carefully dehydrated by boiling it with calcium oxide and treatment with sodium. J. B. T.

Displacement of the Amido- by the Sulphonic Acid-group. By L. LANDSBERG (*Ber.*, 23, 1454).—When freshly prepared cuprous hydroxide is warmed with a large quantity of sulphurous acid, and the warm mixture poured into a solution of diazobenzene sulphate, a rapid evolution of gas sets in and benzenesulphonic acid is formed; the yield is about one-fifth of the aniline employed. F. S. K.

Aromatic Sulphonamic Acids. By W. TRAUBE (*Ber.*, 23, 1653—1657; compare Wagner, Abstr., 1886, 708).—Anilinesulphonic acid is formed by heating aniline with chlorosulphonic acid, or sulphuric anhydride; but if the aniline is dissolved in chloroform or benzene, the solution well cooled, and the chlorosulphonic acid added gradually, a hydrogen-atom of the amido-group is replaced, *phenylsulphonamic acid* being obtained. The free acid could not be isolated, as the aqueous solution readily undergoes decomposition on evaporation. The *barium salt*, $Ba(NHPh\cdot SO_3)_2$, is prepared by treating aniline (3 mols.) with chlorosulphonic acid (1 mol.) as above; the product is poured into water, and treated with barium hydroxide; on evaporating the clear aqueous solution, the barium salt separates in lustrous plates, or long needles, which do not melt. The compound is unaffected by boiling with water, but the addition of a few drops of acid causes its decomposition into aniline and sulphuric acid. The *potassium* and *sodium salts* are obtained from the barium salt by the action of potassium or sodium sulphate.

Barium orthotoluenesulphonamate is prepared from orthotoluidine by the method described. It crystallises from water in lustrous plates, which have no melting point. The free acid could not be obtained in a crystalline form.

Barium metaxylenesulphonamate is prepared from metaxylidine; its properties are very similar to those of the barium salts described above. J. B. T.

Synthesis of Indene-derivatives. By W. v. MILLER and G. ROHDE (*Ber.*, 23, 1881—1886, and 1887—1902; compare Abstr., 1889, 984).—Ketones, like aldehydes, condense to form indene-derivatives; the only general condition being that the side chain shall not contain a double bond. Metanitroketones of the cinnamic acid series resemble the corresponding aldehydes in their behaviour towards tin and hydrochloric acid. Metanitrobenzalacetone, like metanitrocinnamic aldehyde, yields no indene-derivative, whilst metanitro-orthomethylbenzalacetone gives metamido-$\beta\gamma$-dimethylindene.

γ-Methylindene, $C_6H_4<{CH_2 \atop CMe}>CH$, is obtained by treating benzalacetone with 8 times its weight of concentrated sulphuric acid; after 24 hours, it is poured into water, and distilled in a current of steam, the distillate is extracted with ether, and, after evaporation, the oily residue is purified by distillation; the yield is very small. The *picrate*, $C_{10}H_{10},C_6H_2(NO_2)_3{\cdot}OH$, crystallises in long, orange-yellow, radiating needles melting at 75—76°. Methylindene dissolves in concentrated sulphuric acid with a yellowish-brown colour; the solution exhibits an intense green fluorescence; on adding water, the colour changes to dark yellowish-red, and, finally, becomes red.

Orthomethylbenzylacetone, $CH_2Ph{\cdot}CHMe{\cdot}COMe$, is prepared by distilling a mixture of α-methyl-γ-phenylpropionic acid and calcium acetate; it forms an almost colourless oil boiling at 234—241° (corr.); it undergoes a slight decomposition on distillation at ordinary pressure; no indene-derivative could be obtained from it, and it does not appear to combine with hydrogen sodium sulphite.

Metamido-$\beta\gamma$-dimethylindene, $NH_2{\cdot}C_6H_3<{CH_2 \atop CMe}>CMe$, is obtained by heating metanitro-α-methylbenzalacetone with tin and alcoholic hydrochloric acid; when the reaction is completed, the alcohol is removed and the residue treated with sodium hydroxide and distilled in a current of steam. The compound crystallises in small, lustrous plates melting at 62—63°; it is very soluble, but cannot be recrystallised without undergoing decomposition; it reduces an ammoniacal silver solution, and is very unstable on exposure to light. The *benzoyl*-derivative is deposited in crystalline nodules melting at 198°. *Metamidobenzalacetone* is obtained by the reduction of metanitrobenzalaniline with ferrous ammonium sulphate; it is an oily liquid; the *benzoyl*-derivative, $NHBz{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COMe$, crystallises from benzene in small nodules and melts at 125°. Metamidobenzalacetone yields *metamidobenzylacetone* on treating it with sodium amalgam in acid solution; it is an oily liquid; the *benzoyl* compound,

$$NHBz{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}COMe,$$

melts at 94—95°. No indene-derivative could be obtained from metamidobenzylacetone, thus proving that the influence of the substituting-groups in the α-position does not merely consist in rendering the side chain capable of being reduced.

The power of condensing to form indene-derivatives is not confined to meta-substituted acids, as hitherto supposed; both ortho- and para-compounds are capable of reacting in the same manner; but, as in

the case of aldehydes, this property is greatly dependent on the character of the substituting-groups; the presence of chlorine, bromine, or methyl in the benzene nucleus facilitates the condensation, whilst the amido-group entirely prevents it; as aldehydes acquire the power of forming indene-derivatives in the first instance from the presence of the amido-group, the contrast is sufficiently striking; the difference may, however, be due to the dehydrating agents employed, which are, for aldehydes, tin and hydrochloric acid; for acids, concentrated sulphuric acid.

β-Methylhydrindone, $C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{CO}>CHMe$, is prepared by heating αβ-methylphenylpropionic acid with 12 times its weight of concentrated sulphuric acid for a few moments at 150°; the liquid is rapidly cooled, poured into water, and treated with excess of sodium hydroxide; the solution is distilled in a current of steam, and the distillate shaken with ether; the oily residue remaining, after evaporation of the ether, is finally purified by distillation. The hydrindone is a viscid, colourless liquid boiling, with slight decomposition, at 244—246° (corr.) under a pressure of 719 mm., and at 167—170° at 117 mm.; it has a penetrating odour resembling that of peppermint, and is readily soluble in water, but insoluble in alkalis; a bluish-violet fluorescence is produced on shaking with concentrated sulphuric acid: the yield is 60 per cent. of the propionic acid employed. Phthalic acid is obtained by oxidising the hydrindone with dilute nitric acid. *β-Methylhydrindonephenylhydrazone*, $C_{10}H_{10}N_2HPh$, crystallises from alcohol in small, yellow leaves melting at 116°. *Metabromhydrindone*, $C_6H_3Br<\genfrac{}{}{0pt}{}{CH_2}{CO}>CH_2$, is prepared by heating metabromophenylpropionic acid with concentrated sulphuric acid at 145°. After purification, it crystallises in white needles melting at 122—123°. The yield is 40—50 per cent. *Parabromhydrindone* is obtained in a similar manner from parabromophenylpropionic acid; it melts at 111—112°, and is identical with a compound obtained by Göring (compare Abstr., 1878, 318). Metachloropropionic acid, prepared by the action of sodium amalgam on metachlorocinnamic acid, readily condenses under the influence of sulphuric acid with formation of *metachlorhydrindone*, $C_6H_3Cl<\genfrac{}{}{0pt}{}{CH_2}{CO}>CH_2$ [CH_2·CO·Cl = 1 : 2 : 5], which crystallises from dilute alcohol in white needles melting at 95°, and boiling at 274° without decomposition; it is sparingly soluble in water. The *phenylhydrazone*, $C_9H_7Cl{\cdot}N_2HPh$, is obtained in colourless, lustrous, radiating needles melting at 139°; it readily decomposes on exposure to light. Chlorophthalic acid (m. p. 148°) is the sole oxidation-product of metachlorhydrindone; the *phenylhydrazine salt* of this acid is very sparingly soluble; it crystallises in small, white needles melting at 148°. *Metachloro-α-methylcinnamic acid*, $C_6H_4Cl{\cdot}CH{:}CMe{\cdot}COOH$, is prepared by means of Perkin's reaction; it crystallises from chloroform in thick, colourless prisms melting at 106°. The sodium, copper, and barium salts have been prepared; the last-named crystallises in lustrous scales. On treating the free acid with concentrated sulphuric acid, a substance, which is probably

a chlorindone, is obtained in very small quantity. *αβ-Methylmetachlorophenylpropionic acid* is prepared by the action of sodium amalgam on the corresponding cinnamic acid; it is an oily liquid boiling at 292—296°. *β-Methylmetachlorhydrindone*, $C_6H_3Cl{<}{}^{CH_2}_{CO}{>}CHMe$, is obtained from the previous compound; it is a colourless, strongly refractive, viscid liquid boiling at 265—268°; its odour resembles that of menthol, and it is very sparingly soluble in water. *Paramethylcinnamic acid* is prepared by Perkin's reaction; it crystallises from benzene in fine needles melting at 195·5°, is readily soluble in water, and yields the corresponding propionic acid on reduction with hydriodic acid and phosphorus. *Paramethylhydrindone*,

$$CH_3{\cdot}Me{\cdot}{<}{}^{CH_2}_{CO}{>}CH_2,$$

is obtained from paramethylphenylpropionic acid; it crystallises from light petroleum in white needles melting at 63°. *Metamethylhydrindone*, from metamethylphenylpropionic acid, is deposited from light petroleum in long, white needles melting at 59°. *Metanitro-α-methylcinnamic acid*, $NO_2{\cdot}C_6H_4{\cdot}CH{:}CMe{\cdot}COOH$, is prepared by means of Perkin's reaction; it forms a white powder melting at 197·5°, and is sparingly soluble in light petroleum. *Metamido-orthomethylcinnamic acid* is obtained from the nitro-compound by reduction with ammonium ferrous sulphate; it crystallises in long, light-yellow needles melting at 137°. The *benzoyl-derivative* melts at 190—191°. *αβ-Methylmetamidophenylpropionic acid*, $NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CHMe{\cdot}COOH$, is formed from the amidocinnamic acid by reduction with hydriodic acid and phosphorus; it is a reddish-brown oil. The *benzoyl* compound melts at 147—148°. No indone-derivatives could be obtained from these three acids. J. B. T.

Bidioxymethyleneindigo. By C. LIEBERMANN and F. HABER (*Ber.*, **23**, 1566—1567).—Piperonal was converted into nitropiperonal by the method of Fittig and Remsen; this was dissolved in acetone, and a slight excess of dilute aqueous soda added, when a violet-red, flocculent precipitate of *bidioxymethyleneindigo*,

$$C_2[{<}{}^{CO}_{NH}{>}C_6H_2{<}{}^{O}_{O}{>}CH_2]_2,$$

was formed. This may also be obtained by using pyruvic acid instead of acetone. It is a deep-blue substance, less soluble than indigo. It dissolves in concentrated sulphuric acid, giving a bluish-red solution, which exhibits two absorption-bands, the stronger extending from D to Cαβ, the weaker from E to *b*. When water is added to the solution, the substance is precipitated unchanged. When heated, it gives violet-red vapours. C. F. B.

Condensation of Dichlorether with Cresols. By C. BRÜCKNER (*Annalen*, **257**, 322—330).—Ortho-, meta-, and para-cresol combine with dichlorether, yielding the corresponding *trihydroxytritolylethanes*, $OH{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}CH(C_6H_3Me{\cdot}OH)_2$. The three compounds are all

colourless, amorphous powders, turn reddish on exposure to the air in a moist condition, and are readily soluble in ether, alcohol, glacial acetic acid, ethyl acetate, acetone, and benzene, but only sparingly in carbon bisulphide (the ortho-compound is insoluble), and insoluble in chloroform, water, and light petroleum. The *triacetyl*-derivatives, $C_{29}H_{30}O_6$, are yellowish, amorphous compounds, soluble in alcohol, ether, glacial acetic acid, ethyl acetate, acetone, carbon bisulphide, and chloroform, but insoluble in water, alkalis, and light petroleum. Brownish-violet dyes of the composition $C_{46}H_{46}O_7$ are formed when the trihydroxyditolylethanes are dissolved in acetic acid, and the solutions boiled with ferric chloride; they are dark powders, which decompose at about 200°, and are readily soluble in alkalis, alcohol, ether, glacial acetic acid, acetone, and ethyl acetate, but insoluble in carbon bisulphide, benzene, chloroform, and light petroleum; when boiled with acetic anhydride and sodium acetate, the ortho- and the para-compound yield *triacetyl*-derivatives of the composition $C_{58}H_{58}O_{13}$, whilst the meta-compound seems to yield a mixture of various substances. F. S. K.

Paramidotriphenyl Carbinol. By A. BAEYER and R. LÖHR (*Ber.*, **23**, 1621—1628; compare Tschacher, Abstr., 1888, 375).—Paramidotriphenyl carbinol, the simplest representative of the rosaniline dyes, has not hitherto been prepared; it has now been obtained and is found to correspond in every way with the di- and tri-amido compounds. Although itself colourless, its salts are red; it is a weak base, and probably for this reason does not dye wool or silk.

Paranitrotriphenylmethane is obtained by treating 1 part of paranitrobenzaldehyde with 4 parts of benzene and 4 parts of sulphuric acid. After remaining for 24 hours, the benzene solution is separated from the acid and purified; on evaporating the benzene, the hydrocarbon forms an oily residue, which quickly solidifies. The compound crystallises from alcohol in white plates melting at 93°; on treatment with fuming nitric acid, it yields paratrinitrotriphenylmethane.

Paranitrotriphenyl carbinol is prepared by oxidising paranitrotriphenylmethane with chromic anhydride; the compound is purified by dissolving it in glacial acetic acid and precipitating with water; it melts at 136°.

Paramidotriphenylmethane is completely analogous to orthamidotriphenylmethane. The *hydrochloride* is obtained by treating an alcoholic solution of the nitro-compound with tin and hydrochloric acid; it crystallises from dilute hydrochloric acid in lustrous plates or needles. The *free base* is liberated on adding sodium hydroxide solution to the hydrochloride; it crystallises from light petroleum in short, lustrous needles melting at 83—84°. The *sulphate* and *nitrate* are sparingly soluble in water.

Acetylparamidotriphenylmethane, $CHPh_2{\cdot}C_6H_4{\cdot}NHAc$, is formed on warming the free base with acetic anhydride. On the addition of water, the compound is deposited from glacial acetic acid in bushy aggregates of needles or prisms, melting at 157°.

Acetylparamidotriphenylcarbinol, $OH{\cdot}CPh_2{\cdot}C_6H_4{\cdot}NHAc$, is obtained by cautiously oxidising the preceding compound with chromic an-

hydride. On the addition of light petroleum to a benzene solution, it forms slender, lustrous needles melting at 176°. The acetyl compound is best hydrolysed by dissolving it in glacial acetic acid, and pouring the solution into hot dilute sulphuric acid; the mixture is then boiled for some time, and the base precipitated with an alkali.

Paramidotriphenyl carbinol, $OH\cdot CPh_2\cdot C_6H_4\cdot NH_2$, crystallises from toluene, or from a mixture of ether and light petroleum, in small, colourless nodules, melting at 116°. The *sulphate* is *red*, and forms well developed plates, containing 1 mol. H_2O, which it loses at 100°. The *hydrochloride* crystallises from alcohol in long, red needles, which give up 1 mol. H_2O on heating to 120°. The *platinochloride* is red. The *picrate* is sparingly soluble, and crystallises in coloured needles. By the reduction of paranitrotriphenyl carbinol, a base is obtained, which crystallises from ether in long, well-developed, yellowish, lustrous needles melting at 123—124°. This compound appears to be *paramidobenzophenone*. The *hydrochloride* crystallises in tufts of long, golden-coloured needles. J. B. T.

Displacement of the Methylene Hydrogen-atoms in Deoxybenzoïn and Benzyl Cyanide: New Synthesis of Substituted Quinolines. By M. BUDDEBERG (*Ber.*, 23, 2066—2078).—*Allyldeoxybenzoïn*, $COPh\cdot CHPh\cdot C_3H_5$, is obtained when deoxybenzoïn is treated with sodium ethoxide and allyl iodide. It is a yellowish-brown oil boiling at 335—337°; its benzyl-derivative could not be prepared.

Allylbenzyl cyanide, $CN\cdot CHPh\cdot C_3H_5$, prepared by heating benzyl cyanide at 150—160° with allyl iodide and anhydrous sodium hydrate, is a colourless oil boiling at 260—270°; the yield is very small. When warmed with sodium ethoxide and benzyl chloride in alcoholic solution, it yields small quantities of an oil boiling at 320—330°, which seems to be impure benzylallylbenzyl cyanide,

$$CH_2Ph\cdot CPh(CN)\cdot C_3H_5.$$

Orthonitrobenzyldeoxybenzoïn, $NO_2\cdot C_6H_4\cdot CH_2\cdot CHPh\cdot COPh$, can be obtained by gradually adding a dilute alcoholic solution of sodiodeoxybenzoïn to a cold alcoholic solution of orthonitrobenzyl chloride. It crystallises from alcohol in needles, melts at 100—102°, and is readily soluble in alcohol, ether, glacial acetic acid, &c.; a benzyl-derivative of this compound could not be obtained. The corresponding *para*-compound, prepared in like manner, crystallises from alcohol in needles, melts at 110—112°, and is rather more sparingly soluble in alcohol than the ortho-compound. Orthodinitrostilbene (m. p. 196°), identical with the compound prepared by Bischoff (Abstr., 1888, 1094), is formed when orthonitrobenzyl chloride is added to an alcoholic solution of sodiobenzyl cyanide.

A compound of the composition $C_{21}H_{15}N$, which seems to be *αβ-diphenylquinoline*, is formed when orthonitrobenzyldeoxybenzoïn is reduced with iron powder and hot glacial acetic acid. It separates from alcohol in large, transparent crystals, melts at 95—96°, boils at about 420° without decomposition, and is soluble in most ordinary

solvents. Vapour-density determinations gave results in accordance with the molecular formula given above. The *hydrochloride* crystallises in thin plates, and is decomposed by cold water. The *mercurochloride* crystallises from boiling dilute hydrochloric acid in long needles, and turns yellowish on exposure to the air. The *platinochloride*, $(C_{21}H_{15}N)_2.H_2PtCl_6$, is an orange-yellow, crystalline powder very sparingly soluble in water and alcohol.

Paramidobenzyldeoxybenzoïn, $NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CHPh{\cdot}COPh$, can be obtained by reducing paranitrobenzyldeoxybenzoïn with stannous chloride and hydrochloric acid in boiling alcoholic solution. It crystallises from alcohol in needles, melts at 140—141°, and is readily soluble in the ordinary solvents. The *hydrochloride*, $C_{21}H_{19}N,HCl$, crystallises from dilute alcohol in needles, is very readily soluble in alcohol, and is decomposed by boiling water. F. S. K.

Derivatives of Deoxybenzoïn. By J. EPHRAIM (*Chem. Centr.*, 1890, i, 906; from *Inaug. Diss. Berlin*).—By heating phthalic anhydride with orthocarboxylphenylacetic acid at 190°, *deoxybenzoïnorthodicarboxylic acid*, $COOH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4{\cdot}COOH$, is formed melting at 238—239°. Another substance, melting at 250°, is formed at the same time, and appears to be a double lactone.

Dibenzylorthodicarboxylic acid is obtained from deoxybenzoïnorthodicarboxylic acid by heating the latter with hydrogen iodide and phosphorus. With alcoholic ammonia, *deoxybenzoïnorthoimidodicarboxylic acid*, $C_{16}H_{11}O_3N$, is formed, the constitution of which is not certain. Phosphorus oxychloride abstracts one molecule of water from it, forming the compound $C_{16}H_9O_2N$.

Deoxybenzoïnorthodicarboxylic anhydride is obtained by passing hydrogen chloride into the alcoholic solution of the acid, after which the addition of water causes the formation of a precipitate, which is treated with sodium carbonate. Ethyl iodide, when added to the silver salt suspended in alcohol, causes the formation of the same anhydride. Hydroxylamine reacts with deoxybenzoïnorthodicarboxylic acid, with formation of an *oximidolactone*, $C_{16}H_{11}O_4N$, melting at 229—230°. Sodium amalgam reduces the same acid to the *lactide of hydroxytoluyleneorthodicarboxylic acid*, melting at 201°, from which, by the action of barium hydroxide, followed by silver nitrate, the silver salt is obtained. The free acid could not be prepared. The barium salt crystallises with 2 mols. H_2O. J. W. L.

Isomeric Cuminildioximes. By E. HOFFMANN (*Ber.*, **23**, 2064—2066).—*α-Cuminildioxime*, $C_{20}H_{24}N_2O_2$, separates in colourless crystals when cuminil is warmed with hydroxylamine hydrochloride in methyl alcoholic solution; it melts at 249°, and is almost insoluble in alcohol, ether, and benzene, but readily soluble in soda. The *diacetyl*-derivative, $C_{24}H_{28}N_2O_2$, prepared by treating the dioxime with acetic anhydride in the cold, forms colourless crystals, melts at 127°, and is sparingly soluble in alcohol and glacial acetic acid.

β-Cuminildioxime, $C_{20}H_{24}N_2O_2$, is obtained when the α-compound is heated with alcohol at 140° for 10 to 12 hours. It crystallises from

alcohol in needles, melts at 227°, and is readily soluble in alcohol and soda. The *diacetyl*-derivative is a syrup. F. S. K.

Oximes of Halogen-benzophenones. By K. AUWERS and V. MEYER (*Ber.*, **23**, 2063—2066).—Various compounds are formed when bromobenzophenone is treated with hydroxylamine in alkaline solution, but they have not yet been isolated. Chlorobenzophenone under the same conditions yields at least two isomeric oximes; the one melts at 96—97°, but solidifies again on prolonged heating at 100°, being converted into an isomeride which, after recrystallisation from alcohol, melts at about 155°; the other melts at 155°, and may be identical with the compound (m. p. 148—149°) obtained by Beckmann and Wegerhoff (*Annalen*, **252**, 7). The acetyl- and benzyl-derivatives of these two compounds also differ from one another. F. S. K.

Molecular Weight of the Desaurines. By V. MEYER (*Ber.*, **23**, 1571—1573).—Under the name of "Desaurines," a class of compounds has been described, distinguished by their golden-yellow colour, insolubility, and the formation of a blue-violet solution with concentrated sulphuric acid. They are obtained by the action of thiophosgene, $CSCl_2$, on deoxybenzoïn and analogous compounds, and that obtained from deoxybenzoïn itself has the composition COPh·CPh:CS. Its properties seemed to show that its molecular formula must be a multiple of that given above, and at the request of the author experiments were made by Beckmann on the lowering of boiling point caused when it is dissolved in ethylene bromide, as compared with solutions of benzil and phenyl benzoate in the same solvent. The results corresponded with a molecular weight double of that given above; possibly, therefore, the formula of the substance is $\mathrm{COPh{\cdot}CPh{:}C{<}_{S}^{S}{>}CPh{:}C{\cdot}COPh}$. C. F. B.

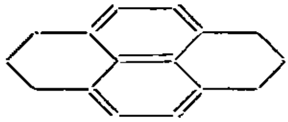
Benzyloxanthranol. By C. BACH (*Ber.*, **23**, 1567—1571).—This substance is obtained as a flocculent precipitate on reducing anthraquinone with zinc-dust, and shaking the filtered alkaline solution in air. Its formula is $\mathrm{CO{<}_{C_6H_4}^{C_6H_4}{>}C(OH){\cdot}CH_2Ph}$. When heated in a reflux apparatus with sodium acetate and acetic anhydride, it yields the *acetyl*-derivative, which forms yellowish needles melting at 281°, soluble in strong sulphuric acid with a yellow colour, and decomposed by long boiling with alcohol, benzyloxanthranol being re-formed. By dissolving the latter substance in strong sulphuric acid, *dehydrobenzyloxanthranol*, $\mathrm{CO{<}_{C_6H_4}^{C_6H_4}{>}C{:}CHPh}$, is obtained. This forms long, yellow needles, which sublime without decomposition. When allowed to remain for a few hours with the calculated quantity of bromine, it takes up two atoms of it and forms *dehydrobenzyloxanthranol bromide* $\mathrm{CO{<}_{C_6H_4}^{C_6H_4}{>}CBr{\cdot}CHBrPh}$, which crystallises from benzene in yellow needles melting at 148°, and soluble in ether, acetic acid, sulphuric acid, and slightly in alcohol, but not in water; its solution

in sulphuric acid is yellowish-red. By boiling it for a long time with alcohol, *bromodehydrobenzyloxanthranol*, $CO<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C:CBrPh$, is obtained. This dissolves easily in alcohol, and with sulphuric acid yields a violet-red solution. It crystallises from alcohol in yellow crystals melting at 254°, and forms yellow needles when sublimed. By heating it with red phosphorus and hydriodic acid in a reflux apparatus, *γ-benzylanthracene*, $C_6H_4<\begin{matrix}C(CH_2Ph)\\|\\CH\text{———}\end{matrix}>C_6H_4$, is formed, and is obtained by extracting the mass with alcohol and precipitating the hydrocarbon by the addition of a little water to the alcoholic extract. It crystallises from alcohol in long, colourless needles which melt at 119°; it dissolves in alcohol, ether, and benzene with a blue fluorescence, whilst its solution in concentrated sulphuric acid is green, and exhibits a red fluorescence. When it is dissolved in carbon bisulphide and treated with bromine (1 mol.), *bromobenzylanthracene*, $C_{21}H_{16}Br$, is formed; on evaporating the solution, this is left as prisms, which are soluble in alcohol, ether, and acetic acid, in benzene with a bluish fluorescence, and in sulphuric acid with a green colour. It crystallises from benzene in yellowish prisms, and decomposes when heated to 113—114°. By dissolving benzylanthracene in sulphuric acid and neutralising with barium carbonate, *barium benzylanthracenemonosulphonate*, $(C_{21}H_{15}SO_3)_2Ba$, is obtained in small, yellowish needles, which in solution exhibit a blue-violet fluorescence. C. F. B.

Action of Methyl Chloride on Naphthalene, and the Constitution of the Hydrocarbon obtained from Carminic Acid. By C. A. Bischoff (*Ber.*, **23**, 1905—1908).—By the action of methyl chloride on naphthalene in presence of aluminium chloride, the author finds, in agreement with Brunel (Abstr., 1884, 1035), that no methylnaphthalene is formed. If the product of the reaction be subjected to distillation, it yields, below 225°, a fraction containing naphthalene; between 225—260°, substances come over which partially solidfy, and have melting points varying from 54° to 70°; between 260—325°, small quantities of oily products distil over, which were not further examined. The residue on distillation in a vacuum yielded two chief fractions, the one boiling below 360°, and the other above 360°. The former fraction was solid, but mixed with oil, and was purified by recrystallisation from alcohol. As soon as the melting point became 179—181°, the crystals were united with those obtained from the second fraction, and the whole recrystallised from alcohol until it became white; it was thus obtained in small plates, sparingly soluble in cold alcohol, acetic acid, and light petroleum, readily in the hot liquids. It was not free from ash, but the analyses appear to show that its formula is $C_{16}H_{10}$ or $C_{16}H_{12}$. It forms a *picrate*, crystallising in long, elastic, orange-yellow needles, which become plastic at 162°, and melt at 181°.

In its properties the hydrocarbon strongly resembles the compound $C_{16}H_{12}$ obtained by Liebermann and Dorp from ruficoccin (Abstr., 1872, 706), and by Fürth from carmine (Abstr., 1884, 84), the melting points and behaviour towards chromic and picric acids agree-

ing almost exactly, so that the two substances are probably identical. The author believes that it is formed from tetramethylnaphthalene (1 . 1′ . 4 . 4′), and that the carbon-atoms are united in the following manner—



an assumption which agrees well with the formula proposed by Liebermann and Dorp for ruficoccin (*loc. cit.*). H. G. C.

Reduction of Naphthalene and Anthracene. By E. BAMBERGER and M. KITSCHELT (*Ber.*, **23**, 1561—1565).—When naphthalene is dissolved in amyl alcohol and treated with sodium, it is almost entirely reduced to *tetrahydronaphthalene*, $C_{10}H_{12}$, which is a colourless, mobile oil boiling at 204·5—205° at 716 mm. pressure, and not solidifying in a freezing mixture. It has an odour like that of naphthalene, its sp. gr. at 17° is 0·978, and it very readily undergoes oxidation. When oxidised at the ordinary temperature with a dilute permanganate solution, it yields orthocarboxyhydrocinnamic acid,

$$COOH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

and hence must have all its four additional hydrogen-atoms in the same ring [$H_4 = 1:2:3:4$]. This tetrahydronaphthalene has moreover been obtained from tetrahydroamidonaphthalene [$NH_2 : H_4 = 1' : 1 : 2 : 3 : 4$] by the diazo-reaction, and probably also in an attempt to displace the amido-group in this substance by the nitro-group by means of Sandmeyer's reaction. It is not, however, identical with the tetrahydronaphthalene obtained by Graebe by treating naphthalene with hydriodic acid and phosphorus, for this yielded phthalic and not orthocarboxyhydrocinnamic acid when oxidised, and when treated with sulphuric acid it yielded a sulphonic acid, the barium salt of which crystallised in tables with $1\frac{1}{2}$ mols. H_2O. The tetrahydronaphthalene obtained by the authors, on the other hand, yielded a *sulphonic acid*, the barium salt of which $(C_{10}H_{11}SO_3)_2Ba$, was anhydrous and crystallised in small, white needles.

Attention is drawn to the fact that naphthalene readily takes up four hydrogen-atoms, whilst anthracene takes up only two, which unite themselves to the middle carbon-atoms. This fact accords best with the hexacentric formulæ for naphthalene and anthracene.

C. F. B.

Action of Chlorine on Quinoneoximes. By T. ZINCKE and L. SCHMUNK (*Annalen*, **257**, 133—155).—Chlorine converts β-naphthaquinone-α-oxime into derivatives strictly analogous to those obtained from β-naphthaquinone (compare Zincke, Abstr., 1888, 158 and 489); its action is quite different from that of bromine, which forms an additive product with the oxime, as has been shown by Brömme (Abstr., 1888, 490).

Chloro-β-naphthaquinone-α-oxime, $C_6H_4{<}{\substack{C(:NOH)\\ CH : CCl}}{>}CO$, is deposited in crystals when the theoretical quantity of chlorine is passed

into a well-cooled chloroform solution of β-naphthaquinone-α-oxime, and the solution is then kept for about 12 hours. It crystallises from hot alcohol in yellowish-red needles, melts at 167—168° with decomposition, and is readily soluble in hot alcohol, glacial acetic acid, chloroform, and benzene; it dissolves in cold concentrated sulphuric acid, yielding a red solution from which it is reprecipitated unchanged on the addition of water. The *sodium* salt, $C_{10}H_5ClNO_2Na$, separates in green plates when soda is added to an alcoholic solution of the oxime; it is moderately easily soluble in water and dilute alcohol, and it gives coloured precipitates with solutions of salts of the heavy metals. Chloro-β-naphthaquinone-α-oxime is decomposed when it is boiled with concentrated hydrochloric or sulphuric acid in glacial acetic acid solution, and, on cooling, chlorhydroxynaphthaquinone (m. p. 214—215°) is deposited; when oxidised with nitric acid in warm acetic acid solution, it yields chloro-β-naphthaquinone and resinous products.

Chlorhydroxynapthaquinoneimide, $C_{10}H_6ClNO_2$, is formed when chloro-β-naphthaquinoneoxime is heated with sulphuric acid (1 vol.) and acetic acid (3 vols.) at a temperature below 80—90°. It crystallises from hot alcohol or hot acetic acid in brownish-red needles, melts at 179—180° with decomposition, and is only sparingly soluble in ether and light petroleum, but more readily in benzene; it dissolves unchanged in cold sodium carbonate, yielding a brownish-red solution, but on warming it is converted into chlorhydroxynaphthaquinone, with evolution of ammonia; soda and acids cause the same decomposition. These reactions show that the compound is not an oxime, and its constitution may therefore be expressed by the formula $C_6H_4<\substack{C(NH)\\CO\cdot CCl}>C\cdot OH$.

Dichloro-β-naphthaquinone-α-oxime, $C_6H_4<\substack{C(:NOH)\\CCl:CCl}>CO$, is deposited in green needles, in the form of the potassium salt, when the trichloronaphthaquinoneoxime described below is dissolved in chloroform, and a slight excess of concentrated potash added to the well-cooled solution; the crystals are separated by filtration and decomposed with dilute hydrochloric acid. It crystallises from hot glacial acetic acid in golden needles, melts at 165—166° with decomposition, and is moderately easily soluble in hot glacial acetic acid, hot alcohol, benzene, and chloroform; it dissolves unchanged in cold concentrated sulphuric acid yielding a red solution, but on warming it is converted into β-chlorhydroxy-α-naphthaquinoneoxime (see below); when warmed with nitric acid in acetic acid solution, it is converted into dichloro-β-naphthaquinone (m. p. 184—185°), identical with the compound obtained from α-amido-β-naphthol.

β-Chlorhydroxy-α-naphthaquinoneoxime, $C_6H_4<\substack{C(:NOH)\\CO-CCl}>C\cdot OH$, is best obtained by warming the dichloroxime with concentrated sulphuric acid as long as hydrogen chloride is evolved, and then pouring the cold solution into water. It crystallises from hot dilute alcohol in long, golden needles, melts at 187—188° with decomposition, and is readily soluble in alcohol, ether, and glacial acetic acid, but more

sparingly in light petroleum; it is soluble in boiling water, and it dissolves in sodium carbonate yielding a reddish-brown solution. This oxime can also be prepared by treating β-chlorhydroxy-α-naphthaquinone with excess of hydroxylamine hydrochloride in alkaline solution, as has lately been shown by Kostanecki (Abstr., 1889, 887), who named the product chloronitrosonaphtharesorcinol.

Trichloro-β-ketohydronaphthalene-α-oxime, $C_6H_4<\begin{matrix}C(:NOH)\\CHCl{\cdot}CCl_2\end{matrix}>CO$, is deposited in crystals when excess of chlorine is passed into a well-cooled chloroform solution of β-naphthaquinone-α-oxime. It crystallises from a mixture of benzene and light petroleum in colourless needles, melts at 185—186° with decomposition, and is moderately easily soluble in alcohol, chloroform, and glacial acetic acid; it turns reddish on long exposure to the air, but it is very stable towards acids.

When the bromo- or the dibromo-β-naphthaquinone-α-oxime described by Brömme (*loc. cit.*) is heated with concentrated hydrochloric acid in acetic acid solution, it is converted into chlorhydroxynaphthaquinone (m. p. 214—215°), and not into bromonaphthaquinone, as stated by him; if sulphuric acid is used in the place of hydrochloric acid, the product is bromhydroxynaphthaquinone (m. p. 196—197°). When β-naphthaquinone-α-oxime is treated with bromine in glacial acetic acid solution, it is converted into bromhydroxynaphthaquinone; Brömme states that bromonaphthaquinone is formed under these conditions. F. S. K.

Azo-colours from α-Naphthylamine, Dimethylaniline, and α-Hydroxynaphthoic Acid. By C. A. BISCHOFF (*Ber.*, 23, 1908—1911).—In order to characterise the shade of the colouring matter obtained from dimethylpiperazine and sulphanilic acid (Abstr., 1889, 1010), the author has prepared the following naphthalene azo-colouring matters.

Dimethylamidobenzene-α-azonaphthalene, $Me_2N{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_7$, is prepared by diazotising a solution of an α-naphthylamine salt in the usual manner, and mixing it with an alcoholic solution of dimethylaniline, the crude colouring matter being purified by alternate treatment with hydrochloric acid and ammonia. It is insoluble in cold water, sparingly soluble in alcohol and ether, readily by chloroform, crystallising from the latter in prisms, which appear black by reflected light, and ruby-red by transmitted light. Its hot aqueous solution becomes wine-red on the addition of hydrochloric acid, yellow with acetic acid, and lemon-yellow with soda. It dissolves in concentrated sulphuric acid, forming a violet-coloured solution, and decomposes about 100°.

By the action of sulphuric acid containing 20·5 per cent. of anhydride, it yields, according to the duration of the reaction and the temperature, three sulphonic acids, the sodium salts of which are readily soluble in water. The first, obtained by heating for 10 minutes at 110—112°, has a yellow colour; the second, which is formed at 116—120°, has an orange colour; and the third, obtained by heating for an hour at 125°, a pure brown.

α-Naphthylazo-α-hydroxynaphthoic acid, $C_{10}H_7{\cdot}N_2{\cdot}C_{10}H_5(OH){\cdot}COOH$,

is best prepared by pouring a cold solution of diazonaphthalene chloride in a thin stream into a well-cooled solution of hydroxy-naphthoic acid in sodium carbonate. The colouring matter is recrystallised from acetic acid. This reaction has also been carried out by Nietzki and Guitermann (Abstr., 1887, 732), but they were unable to get any concordant analyses of the compound. The same difficulty was also experienced in this case, but, finally, by very careful combustion, numbers were obtained agreeing closely with the above formula. It forms golden-yellow plates, which melt at 198° with decomposition, and are insoluble in cold water, sparingly soluble in ether, benzene, and chloroform, readily in acetic acid and acetone. It is not decomposed by boiling dilute acids, and dissolves in concentrated sulphuric acid, forming a deep blue solution from which water precipitates it in green floccules. The neutral salts have a deep red colour, and are readily soluble in water, whilst the acid salts are yellow, and less soluble in cold water. The acid sodium salt does not colour unmordanted cotton, but in an alkaline bath dyes wool a fiery orange-yellow. H. G. C.

Sulphonation of Aniline and Naphthylamine with Potassium Hydrogen Sulphate. By C. A. Bischoff, A. Sienecki, and H. Brodsky (*Ber.*, **23**, 1912—1914).—When aniline is heated with potassium hydrogen sulphate (2 mols.) at 200—240°, sulphanilic acid is formed in quantities varying from 8 to 19 per cent., the latter yield being obtained at 200—220°. α-Naphthylamine yields from 15—18 per cent. of the monosulphonic acid, the most favourable temperature being 230°, whilst with β-naphthylamine 60 per cent. of the monosulphonic acid may be thus obtained.

If a mixture of powdered α-naphthylamine (1 part) and potassium hydrogen sulphate (3 parts) be made into thin cakes, then heated to 60—80°, and pressed between hot plates, and the cakes heated for 3 hours at 200°, 50 per cent. of the α-monosulphonic acid may be obtained. According to Bayer and Duisberg, the product from α-naphthylamine is ordinary α-naphthionic acid, and that from β-naphthylamine, β_1-β_3-naphthionic acid mixed with traces of β-naphthylamine-δ-sulphonic acid. H. G. C.

Diazosulphonic Acids. By G. Tobias (*Ber.*, **23**, 1628—1634).—The conversion of diazosulphonic acids into the corresponding chlorosulphonic acids, by the action of cuprous chloride on a hydrochloric acid solution (Sandmeyer's reaction) is frequently incomplete on account of the sparing solubility of the chlorinated compounds in concentrated hydrochloric acid. The addition of water causes the reaction to proceed until the diazo-compound is entirely decomposed; it is also found that a mere trace of cuprous chloride is sufficient to bring about the change.

Tarnished copper foil has the same effect. An evolution of nitrogen takes place if a little *cuprous oxide* is added to the diazo-compound dissolved in any one of the following acids, namely, nitric, sulphuric, acetic, formic, or in ethyl or methyl alcohol, or even in pure water.

In the case of water, the reaction proceeds at the ordinary temperature, but the actual change which occurs has not been ascertained.

Under certain conditions, if the solvent is 50 per cent. formic acid, hydrogen is substituted for the diazo-group—hydrogen sodium diazonaphthalenedisulphonate, for example, yields the corresponding naphthalenedisulphonic acid; a considerable quantity of carbonic anhydride is evolved during the experiment, showing that part of the reduction is effected at the cost of the formic acid.

The action of ethyl alcohol is similar to that of formic acid; the diazo-compound is reduced, and a portion of the alcohol oxidised to aldehyde. Cuprous chloride acts like cuprous oxide, if the solvent is water, alcohol, or formic acid. J. B. T.

Nutmeg Oil and Mace Oil. By F. W. SEMMLER (*Ber.*, **23**, 1803—1810).—A sample of commercial nutmeg oil examined was found to contain nothing but a mixture of terpenes, and its study was abandoned, as these substances are now being investigated by several chemists. It was colourless, and had a sp. gr. of 0·8611 at 15°.

A sample of mace oil was then examined, of sp. gr. 0·9309 at 14°. It had a yellow colour, and contained a considerable quantity of oxygen. With alcoholic ferric chloride, it gave a green colour. It was fractionated under 10 mm. pressure. 53 per cent. passed over below 70°, and was a mixture of the same terpenes as are contained in nutmeg oil. 15 per cent. more came over between 70° and 114°, and doubtless contained myristicol; this fraction is to be examined later. The portion boiling above 114° was practically identical with an oil bought under the name of "high-boiling portions of mace oil." By treating this cautiously with sodium in a vacuum, and distilling the product, a clear homogeneous oil was obtained, boiling at 142—149° under 10 mm. pressure, and of sp. gr. 1·1501 at 25°. When cooled, it forms white needles which melt at 30·25°. Analysis and vapour density point to the formula $C_{12}H_{14}O_3$. It has been named *myristicin*, and it is present as such in the commercial oil. When carefully treated with bromine, it takes up two atoms, yielding *dibromomyristicin*, $C_{12}H_{14}Br_2O_3$, which forms white aggregates of needles melting at 105°. It also takes up chlorine and iodine. Hence, it probably contains a radical of the allyl series. When heated with zinc-dust, it yields benzene, and as it is not acted on by sodium, it is probably an ether, the oxygen-atoms being united both to the benzene ring and to fatty radicals.

Beside myristicin, the crude oil also contains a phenol-like substance, which causes a green colour with ferric chloride, and which oxidises readily in the air, turning dark green. C. F. B.

Ethyl Camphorylmalonate. By J. WISLICENUS and H. WINZER (*Annalen*, **257**, 298—321).—*Ethyl camphorylmalonate*,

$$\begin{array}{l} C_8H_{14} \\ | \\ CO{\cdot}O \end{array}\!\!>C(COOEt)_2,$$

is obtained when camphoric anhydride (1 mol.) or camphoryl dichloride (1 mol.) is treated with ethyl sodiomalonate (2 mols.), and

the mixture heated for a long time to complete the reaction; the whole is then treated with water, and the insoluble oil separated and kept for some time, whereon the new compound is deposited in crystals. It separates from ether in well-defined crystals, melts at 82°, boils at 284° (corr.) under a pressure of 40 mm. without decomposition, and at about 360° under the ordinary pressure with slight decomposition; it is readily soluble in ether, alcohol, chloroform, acetone, carbon bisulphide, and glacial acetic acid, but only sparingly in hot light petroleum, and is insoluble in water. Compounds analogous to ethyl phthalyldimalonate and ethyl phthaloxydimalonate (compare Wisliceuus, Abstr., 1888, 149) are not obtained by the action of ethyl sodiomalonate on camphoryl dichloride.

Hydrocamphorylmalonic acid, $COOH\cdot C_8H_{14}\cdot CH_2\cdot CH(COOH)_2$, is formed when the preceding compound is dissolved in aqueous alcohol and sodium added to the well-cooled solution, which is kept slightly acid by the frequent addition of dilute sulphuric acid. The decanted alcoholic solution is then evaporated, the precipitated oil redissolved by adding soda, the solution mixed with copper sulphate, and the precipitate, which seems to consist of a mixture of the copper salts of ethyl dihydrogen and diethyl hydrogen hydrocamphorylmalonate, separated by filtration; the filtrate is acidified, the precipitated hydrocamphorylmalonic acid separated and recrystallised from a mixture of hot alcohol and benzene. It melts at 178°, and is soluble in ether, alcohol, and hot water, but only very sparingly in cold water and benzene; silver, lead, ferric, and mercurous salts produce precipitates in its neutral aqueous solution, but the copper, ferrous, zinc, and barium salts are readily soluble in water.

Hydrocamphorylacetic acid, $COOH\cdot C_8H_{14}\cdot CH_2\cdot CH_2\cdot COOH$, is obtained by heating the malonic acid derivative until the evolution of carbonic anhydride is at an end; it crystallises from hot water in colourless plates, melts at 141—142°, and is readily soluble in ether, alcohol, and benzene.

Ethyl hydrocamphorylmalonate, $C_{19}H_{32}O_6$, is obtained when the mixture of insoluble copper salts referred to above is decomposed with hydrochloric acid, the oily acids converted into their silver salts, the latter heated with ethyl iodide, and the product fractionated under reduced pressure in order to separate it from a compound of lower boiling point (see below). It is a colourless oil boiling at 253—255° (80 mm.), and is insoluble in water.

Ethyl dihydrogen hydrocamphorylmalonate, $C_{15}H_{24}O_6$, can be prepared by treating the ethyl salt just described with excess of sodium ethoxide in alcoholic solution, and decomposing the crystalline salt which is deposited with hydrochloric acid. It crystallises from hot water in colourless needles, melts at 136—138°, and decomposes at a higher temperature with evolution of carbonic anhydride.

Camphoryldiamide, $C_8H_{14}{<}\begin{matrix}C(NH_2)_2\\CO\text{---}O\end{matrix}{>}$, is gradually deposited in colourless crystals when an ethereal solution of ethyl camphorylmalonate is saturated with ammonia, and then kept for some time. It crystallises from a mixture of alcohol and light petroleum in large prisms, melts at 192—193°, and is readily soluble in alcohol, but

insoluble in ether, chloroform, benzene, and light petroleum; it dissolves freely in water, and on evaporating the solution at 100°, it separates again unchanged. The camphoryldiamide described by Moitessier (*Annalen*, **120**, 253) must have been a very impure substance.

Camphorylimide, $C_8H_{14}<\genfrac{}{}{0pt}{}{C(NH)}{COO}>$, is precipitated when the diamide is boiled with soda, and the solution acidified; it can also be obtained by heating camphoric anhydride with a saturated alcoholic solution of ammonia at 160°. It crystallises in plates, sublimes at 120°, melts at 241—242°, and is readily soluble in ether, alcohol, and hot water, but only sparingly in light petroleum and cold water. This compound has been previously prepared by Laurent (*Annalen*, **60**, 329), and by Ballo (*ibid.*, **197**, 332), but only in an impure condition.

An *acid* of the composition $C_{11}H_{18}O_3$, probably *acetocamphenylcarboxylic acid*, $COMe \cdot C_8H_{14} \cdot COOH$, is formed, together with camphoric acid, malonic acid, and carbonic anhydride, when ethyl camphorylmalonate is boiled with a concentrated solution of barium hydroxide. The whole is boiled with water, the solution filtered from barium carbonate, and concentrated by evaporation to precipitate the barium malonate; the filtrate is then further evaporated, mixed with alcohol, and ether gradually added to the solution, whereon the barium camphorate is first precipitated in crystals, and, finally, the barium salt of the new acid is deposited as a colourless syrup, which, however, gradually solidifies. The free acid crystallises from a mixture of benzene and light petroleum in rhombic prisms, melts at 95°, and is soluble in hot water, ether, alcohol, and benzene, but almost insoluble in cold water and light petroleum; it separates from hot water in the form of an oil, which gradually solidifies to a mass of plates melting at 68—69°. The *ethyl* salt, $C_{11}H_{17}EtO_3$, is produced, together with carbonic anhydride, malonic acid, and ethyl hydrogen camphorate, when an alcoholic solution of ethyl camphorylmalonate is mixed with sodium ethoxide, and kept for about eight days; the solution is then neutralised with dilute hydrochloric acid, the precipitated oil extracted with ether, mixed with a little dilute soda, distilled with steam, dried, and fractionated. It can also be obtained by treating the silver salt of the acid (m. p. 95°) described above with ethyl iodide. It boils at 270—271°, has a slight odour of camphor, and is identical with the low-boiling compound obtained in fractionating ethyl hydrocamphorylmalonate (see above). The *silver* salt, $C_{11}H_{17}AgO_3$, was prepared from this low-boiling compound. The *oxime*,

$$COOH \cdot C_{10}H_7 \vdots N \cdot OH,$$

obtained by treating the acid with hydroxylamine hydrochloride and sodium carbonate in dilute alcoholic solution, crystallises in colourless needles, melts at 166°, and is soluble in ether, alcohol, and hot water, but only sparingly in cold water.

A dicarboxylic *acid* of the composition $C_{21}H_{32}O_4$, is formed with evolution of carbonic anhydride when ethyl camphorylmalonate is heated with concentrated sulphuric acid, and on the addition of

water it is precipitated in colourless crystals; it is also obtained in the form of the sodium salt when ethyl acetocamphenylcarboxylate is boiled for several hours with an alcoholic solution of sodium ethoxide. It crystallises from ether in prisms, melts at 224°, and is readily soluble in alcohol, benzene, and hot water, but more sparingly in light petroleum and ether; it sublimes readily under reduced pressure, and in its neutral aqueous solutions silver, copper, ferric, and mercury salts produce a precipitation. F. S. K.

Amethylcamphophenosulphone and a Nitro-colouring Matter derived from it. By P. CAZENEUVE (*Compt. rend.*, **110**, 961—964).—*Amethylcamphophenolsulphone*, $C_9H_{12}O(SO_2)\cdot(OH)_2$, obtained in the manner already described (this vol., p. 791), forms large, white plates which resemble cholesterin. It dissolves in water, but is less soluble in alcohol, and is insoluble in benzene, ether, chloroform, and carbon bisulphide. It does not melt, is optically inactive, is neutral to litmus and methyl-orange, and does not decompose carbonates. It has a phenolic function, and with ferric chloride gives a deep blue coloration which is destroyed by acids and alkalis. With 1 mol. of potassium hydroxide, it develops 7 Cals., but there is no further thermal disturbance on adding more alkali, although the compound contains two hydroxyl-groups, and one of them must therefore have a secondary alcoholic function. Barium hydroxide yields a precipitate of the composition $C_9H_{12}O(SO_2)\colon O_2Ba$, but no precipitate is formed with lime-water, starch-paste, gelatin, albumin, tartar emetic, or salts of mercury, zinc, or copper. The compound precipitates salts of lead, quinine, cinchonine, aconitine, strychnine, and brucine, but does not precipitate morphine or theïne. It reduces boiling solutions of gold chloride or ammonio-silver nitrate, but not platinic chloride. When fused with potash at 300°, it loses its sulphur and yields a phenol.

Acetic anhydride yields a monacetic derivative of the composition $C_9H_{12}O(SO_2)(OH)\cdot OAc + 2H_2O$, very soluble in water and alcohol. It does not melt without decomposition, gives no coloration with ferric chloride, and no precipitate with barium hydroxide, and is easily saponified. A di-acetic derivative with similar properties is obtained by boiling the compound with acetic anhydride and sodium acetate.

When the compound is heated for a long time on the water-bath with phenylhydrazine, it yields a liquid which is difficult to purify, but the formation of which proves that the compound retains the ketonic group of the camphor.

If 1 part of the compound is added gradually to 5 parts of fuming nitric acid cooled to 0—10°, it dissolves without evolution of gas, and on mixing with ice-cold water, the compound

$$C_9H_8(NO_2)_3O(SO_2)(OH)\cdot ONO_2$$

is precipitated. It crystallises from alcohol in beautiful, yellow needles which melt at 87°, solidify at 80°, and boil above 200° with partial decomposition. It is only slightly soluble in water, but more soluble in alcohol, has a slightly piquant but not bitter taste, deto-

nates when thrown into a red-hot crucible. It is bibasic, and yields orange-yellow crystallisable salts, all of which are soluble. The barium salt crystallises with 2 mols. H_2O, which it loses in a vacuum or at 100°, and acquires a red colour, but absorbs water again on exposure to air.

The nitro-compound and all its salts dye wool and silk a magnificent yellow or orange-yellow without any mordant. It is the first nitro-colouring matter of the terebene group. C. H. B.

Distillation of Rosin in a Vacuum. By C. A. BISCHOFF and O. NASTVOGEL (*Ber.*, **23**, 1919—1924).—If rosin be distilled under diminished pressure, the products obtained are less numerous and more readily separated than when the distillation is carried out at the ordinary pressure. By repeated fractionation of the distillate under 30 mm. pressure, two chief fractions were obtained, that formed in larger quantity boiling at 248—250°; this, on remaining for a short time, solidifies to a colourless, brittle, microcrystalline mass, which is insoluble in water, but dissolves readily in ether and alcohol. It has the composition $C_{40}H_{58}O_3$, rotates the plane of polarisation in alcoholic solution to the right ($[\alpha]_D = 63°$), and behaves in all respects as an anhydride. It dissolves on warming with caustic potash, the solution on acidification with acetic acid yielding the corresponding acid, which melts at 60·5—62·5°, and has the composition $C_{20}H_{30}O_2$. It is, therefore, isomeric with sylvic acid, and may be termed isosylvic acid, the above compound, $C_{40}H_{58}O_3$, becoming then isosylvic anhydride. The second fraction boils at 218—220° under 30 mm. pressure, and appears to be a diterpene having the composition $C_{20}H_{32}$. It is probably identical with Deville and Ribau's colophene. H. G. C.

Peucedanin. By A. JASSOY (*Chem. Centr.*, 1890, i, 766; from *Apoth. Zeit.*, **5**, 150).—This bitter is *oreoselon methyl ether*, $C_{14}H_{11}O_3{\cdot}OMe$. Bromine combines with oreoselon, forming bromoreoselon, and in the same manner it reacts with peucedanin, forming the same compound, the methyl-group being eliminated. Nitric acid forms *nitrooreoselon*, $C_{14}H_{11}(NO_2)O_4$, with both oreoselon and with peucedanin; styphnic acid is formed at the same time. Organic acid anhydrides do not react with peucedanin as they do with oreoselon, but acid chlorides form with peucedanin the same compounds that they do with oreoselon, methyl chloride being separated. J. W. L.

Ostruthin. By A. JASSOY (*Chem. Centr.*, 1890, i, 766; from *Apoth. Zeit.*, **5**, 150).—The bitter, ostruthin, noticed by Gorup-Besanez in the young rhizome of *Imperatoria ostruthium*, has the formula $C_{18}H_{20}O_3$, according to the author's researches, and he finds that it does not contain any methoxyl-group, but a hydroxyl-group of the nature of a phenol. Acid radicles can be readily introduced into this group, and the acetyl-, propionyl-, butyryl-, and benzoyl-ostruthins were prepared. Acid chlorides decompose ostruthin. The author could not find peucedanin in the roots of *Imperatoria ostruthium*. J. W. L.

New Method of Formation of Pyrroline-derivatives. By A. HANTZSCH (*Ber.*, **23**, 1474—1476).—Ethyl 2 : 5-dimethylpyrrolinecarboxylate (m. p. 116—117°), identical with the compound described by Knorr (*Ber.*, **15**, 1558), is formed when concentrated ammonia is gradually added to a mixture of chloracetone (1 mol.) and ethyl acetoacetate (1 mol.); the yield is very small. F. S. K.

Action of Hydroxylamine on Pyrroline-derivatives. By G. CIAMICIAN and C. U. ZANETTI (*Ber.*, **23**, 1787—1793).—When an alcoholic solution of 1-ethylpyrrol and hydroxylamine hydrochloride is boiled with sodium carbonate, succinaldoxime, $C_2H_4(CH{:}N{\cdot}OH)_2$, is formed, together with ethylamine. This shows that in this and similar reactions it is the imido-group of the pyrroline, substituted or otherwise, which goes to form ammonia or an amine.

By treating 2 : 4-dimethylpyrroline with hydroxylamine, *α-methyllevulindioxime*, $OH{\cdot}N{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}CMe{:}N{\cdot}OH$, was obtained. This substance forms yellowish needles or prisms which melt at 87—90° to a liquid of the same colour. It dissolves easily in alcohol and water, sparingly in ether. It reduces Fehling's solution and ammoniacal silver nitrate. When treated with sodium ethylate, it yields a *disodium compound*, $ONa{\cdot}N{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}CMe{:}N{\cdot}ONa$, which is an easily decomposable, yellowish-white powder little soluble in alcohol or ether. When reduced with sodium and alcohol, it yields *αβ′-dimethyltetramethylenediamine*, $NH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}NH_2$. This is a clear, colourless liquid boiling at 175°, fuming in the air, and having a penetrating, ammoniacal odour. It forms a normal *oxalate*, $C_4H_6Me_2(NH_2)_2,C_2H_2O_4$, in fine, white needles melting at 244° and sparingly soluble in alcohol. The *platinochloride*, $C_6H_{16}N_2,H_2PtCl_6$, forms orange-yellow crystals moderately soluble in water; the *aurochloride* forms yellow needles easily soluble in water.

When 2 : 5-methylphenylpyrroline was treated with hydroxylamine hydrochloride and potassium carbonate in alcoholic solution, *acetophenoneacetonedioxime*, $OH{\cdot}N{:}CPh{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}N{\cdot}OH$, melting at 108°, was obtained in small needles, and was identified with the substance formed when acetophenone is treated with hydroxylamine. It dissolves easily in alcohol, acetic acid, and ether, very sparingly in water and light petroleum; it dissolves in caustic alkalis, but is reprecipitated on the addition of acids.

The following table gives the results of experiments hitherto made on the action of hydroxylamine on pyrroline-derivatives. It will be seen that the ease with which these yield oximido-derivatives depends both on the nature and on the position of the substituting radicles:—

Pyrroline. Yield of succinaldoxime, 35 per cent.

2 : 5-*Dimethylpyrroline.* Yield of acetonylacetonedioxime, 90 per cent.

2 : 4-*Dimethylpyrroline.* Yield of α-methyllevulindioxime, 55 per cent.

2 : 5-*Methylphenylpyrroline.* Yield of acetophenoneacetonedioxime, 25 per cent.

1-*Ethylpyrroline.* Yield of succinaldioxime, 20 per cent.

1-*Phenylpyrroline*, 2 : 5-*diphenylpyrroline*, *tetraphenylpyrroline*, *methyl 2-pyrrolinecarboxylate*, *ethyl* 2 : 4-*pyrrolinedicarboxylate*, and also

indole, *thiophen*, and 2 : 5-*dimethylthiophen* are not acted on by hydroxylamine. C. F. B.

Action of Ethyl Oxalate on Pyrroyl Methyl Ketone. By A. ANGELI (*Ber.*, **23**, 1793—1797).—When a cooled alcoholic solution of 2-acetylpyrroline (1 mol.) is treated with ethyl oxalate (1 mol.) in the presence of sodium ethoxide, *ethyl pyrroylpyrotartrate*, $C_4NH_4\cdot CO\cdot CH_2\cdot CO\cdot COOEt$, is formed. It is obtained by saturating the cooled mixture with carbonic anhydride and recrystallising the crystalline precipitate from boiling benzene. It forms brilliant, pale-yellow plates, melting at 123°, and dissolving easily in alcohol and benzene, sparingly in water, and hardly at all in light petroleum. It has feebly acid properties, and gives a green, crystalline precipitate with copper acetate and a green colour with ferric chloride; its benzene solution has a faint green fluorescence. The free acid cannot be obtained from it, as it is decomposed by caustic alkalis.

When treated with alkaline carbonates, or ammonia, it yields the *imineanhydride* of *pyrroylpyrotartaric acid*, $CH\begin{cases}CH{:}C\cdot CO\cdot CH_2 \\ CH\cdot N\cdot CO\cdot CO\end{cases}$, which was also formed in the original reaction, in addition to ethyl pyrroylpyrotartrate, and could be obtained from the mother liquor of the latter by acidifying it with hydrochloric acid. A molecular weight determination by Raoult's method corresponded with the above formula. When crystallised from benzene, it forms yellow needles which decompose at 250° without melting. It dissolves easily in alcohol and acetic acid, sparingly in benzene, and not at all in light petroleum. With water, it gives an unstable solution which is coloured reddish-brown by ferric chloride. It has acid properties, and decomposes solutions of alkaline carbonates, giving orange-yellow solutions.

When ethyl pyrroylpyrotartrate is treated with excess of hydroxylamine hydrochloride, an *anhydride* of *ethylpyrroylisonitrosopropionate* $CH\begin{cases}CH{:}C\cdot CO\cdot CH_2 \\ CH\cdot N\cdot N{=}C\cdot COOEt\end{cases}$, is obtained, which when purified, crystallises from alcohol in white needles melting at 123—124°. When treated with aqueous alkalis, it readily yields the corresponding *acid*, which, when purified, crystallises from alcohol in brilliant, white needles melting with decomposition at 179°. It dissolves easily in alcohol, sparingly in benzene and chloroform, and not at all in water. With strong nitric acid, it gives a green colour; with sulphuric acid and dichromate, a red colour. A solution of its ammonium salt gives, with mercuric chloride, zinc chloride, and lead acetate, white precipitates, soluble in the case of the last two salts on warming the solution; with ferric chloride, a yellow precipitate turning brown when warmed; with silver nitrate, a yellow; with copper sulphate, a green precipitate; and with nickel sulphate, no precipitate. C. F. B.

Compounds of Tertiary Amines with Acetic Acid and its Homologues. By J. A. GARDNER (*Ber.*, **23**, 1587—1594).—Mixtures were made of various tertiary bases with acids of the acetic acid

series, and the mixture in each case subjected to distillation. In several cases it was found that the greater part of the mixture distils at an approximately constant temperature, higher than the boiling point of either of its constituents, and that this fraction has a constant composition. These liquids of constant boiling point have an acid reaction, mix with water in all proportions, and are decomposed by caustic alkalis with liberation of the base; they are not simple acetates, but have a more or less complex composition. They cannot be obtained absolutely pure, as they always decompose somewhat when distilled. Indeed, it was found in most cases, by vapour-density experiments, that the liquid is completely dissociated into base and acid when it passes into the state of vapour. Below are given the boiling points and composition (ratio of mols. of base to mols. of acid) of the fractions of constant boiling point in the case of the mixtures experimented with.

Mixture.	Boiling point.	Composition. Mols. base.		Mols. acid.
Pyridine and acetic acid......	139—140°	2	:	3
Picoline and acetic acid.......	145—148	2	:	3
Triethylamine and acetic acid .	162°	1	:	4
Pyridine and formic acid	148—150	1	:	3
Picoline and formic acid	156—159	1	:	3
Pyridine and propionic acid ...	148—150	1	:	3

Quinoline, dimethylaniline, and aniline were also experimented with, but on distilling mixtures of either of these substances with an acid, decomposition took place, and no fraction of constant boiling point was obtained. C. F. B.

Pyridineorthocarboxylic Acids. By H. STRACHE (*Monatsh.*, 11, 133—148; compare Abstr., 1889, 1016).—When a solution of the anhydride of cinchomeronic acid ($\beta\gamma$-pyridinedicarboxylic acid) in benzene is treated with a large excess of dry gaseous ammonia, a voluminous white precipitate of the ammonium salt of cinchomeronamic acid, $CONH_2{\cdot}C_5NH_3{\cdot}COONH_4$, is formed. It is exceedingly soluble in water, commences to sinter at 50—60°, and melts at 228—229°; the corresponding silver salt crystallises from hot water, in which it is only slightly soluble, in microscopic needles; the free acid is obtained by the action of hydrogen sulphide on a solution of the silver salt, and, on evaporating its aqueous solution, first forms hydrogen ammonium cinchomeronate, which decomposes into cinchomeronic acid and ammonia.

Cinchomeronimide, $C_5NH_3{<}{\substack{CO\\CO}}{>}NH$, is obtained by heating the ammonium salt of cinchomeronamic acid at 120°, in an air-bath, or by heating neutral ammonium cinchomeronate. It melts at 229—230°, sublimes readily, forming dendritic masses of long needles, and crystallises from alcohol in felted masses of microscopic needles. It is only slightly soluble in ether and chloroform, but dissolves readily in water, with partial decomposition, forming cinchomeron-

amic acid, hydrogen ammonium cinchomeronate, and free cinchomeronic acid, and yields a sodium-derivative when treated with sodium ethylate.

Cinchomerondianilide, $C_5NH_3(CO\cdot NHPh)_2$, is obtained by gradually dissolving cinchomeronic acid in four times its weight of aniline; on crystallisation from dilute alcohol, it forms small, pale-yellow needles melting at 199—206°. It is insoluble in water, but dissolves readily in benzene and chloroform, with difficulty in ether and in water containing hydrochloric acid. When heated above its melting point, aniline escapes with formation of *cinchomeronphenylimide*, $C_5NH_3<\substack{CO\\CO}>NPh$, a substance which crystallises in long, yellow needles, melts at 212—215·5°, is very soluble in hot alcohol, benzene, and chloroform, scarcely soluble in hot water, cold alcohol, and ether, and insoluble in dilute hydrochloric acid and aqueous potash.

Cinchomeronic acid dissolves readily in boiling phenylhydrazine, yielding a diphenylhydrazine compond, $C_5NH_3(CON_2H_2Ph)_2$, which forms yellow, crystalline flocks, soluble in dilute acids and alkalis, and crystallising from alcohol in masses of slender needles. When heated, it loses a molecule of phenylhydrazine with formation of a monophenylhydrazine compound, which melts at above 260°, sublimes readily, is sparingly soluble in water, ether, benzene, and chloroform, dissolves readily in alcohol and dilute acids and alkalis, and has the constitution

$$\begin{matrix}NPh\cdot CO\\ | \\ NH\cdot CO\end{matrix}>C_5NH_3, \quad \text{or} \quad NHPh\cdot N<\substack{CO\\CO}>C_5NH_3.$$

G. T. M.

Orthoparadimethylquinoline-α-Aldehyde. By G. PANAJOTOW, (*Ber.*, **23**, 1471).—Orthoparadimethylquinoline-α-aldehyde

$$[COH : N : Me_2 = 3 : 4 : 2' : 4']$$

is formed when orthoparadimethylquinoline-α-acrylic acid hydrochloride (5 grams) is dissolved in sodium carbonate, the solution diluted with water (250 grams), covered with a layer of benzene (125 grams), cooled to 0°, and a solution of potassium permanganate (5 grams) gradually added with constant shaking; the yield is 10 per cent. of the theoretical. It crystallises from light petroleum in yellowish plates, melts at 107°, and is readily soluble in alcohol, ether, and acids, but only sparingly in water and light petroleum.

F. S. K.

Polymerisation of Nitriles: Cyanalkines (Metadiazines). By R. SCHWARZE (*J. pr. Chem.* [2], **42**, 1—18; compare Abstr., 1889, 114, 360, 577, 683, 685).—When sodium ethoxide (1 mol.) and ethyl cyanide (3 mols.) are heated together at 130° for 3—4 hours, amidomethyldiethylmetadiazine (cyanethine) is obtained, the yield being about 66 per cent. In the same way, amidodimethylmetadiazine (cyanomethine) is obtained from methyl cyanide and sodium ethoxide; in this case the yield is 35 per cent. When isopropyl cyanide (3 mols.) and sodium ethoxide were heated together at 160—170°, the mass

became solid, and an uninvestigated nitrogenous substance was obtained, but no cyanalkine was formed. When propyl cyanide (15 grams) and sodium ethoxide (7 grams) are heated together at 170°, amidomethyldipropylmetadiazine (cyanopropine, Abstr., 1888, 800; 1889, 684) is obtained.

Amidodimethylmetadiazine is also formed (62 per cent.) when sodium methoxide (5·5 grams) and methyl cyanide (15 grams) are heated together at 130°, and amidomethyldiethylmetadiazine when sodium methoxide and ethyl cyanide are similarly treated at 160° Sodium isobutoxide (7 grams) and ethyl cyanide (12 grams), heated together at 190°, yielded amidomethyldiethylmetadiazine (21 per cent.) and an *isomeride* of the same; this was a colourless oil, which had a characteristic odour, and solidified after a time; the *platinochloride* from this oil crystallised in yellowish-red needles. No change occurred when sodium phenoxide and ethyl cyanide were heated together.

Amidomethyldiphenylmetadiazine (Abstr., 1889, 578; this vol., p. 68) is obtained when sodium ethoxide (4 grams), ethyl cyanide (4·8 grams), and phenyl cyanide (9 grams) are heated together at 180°. The same substance is produced when sodium, ethyl cyanide, and phenyl cyanide (equal mols.) are mixed together in a reflux apparatus; the *hydrochloride*, *sulphate*, two *chromates* $(C_{17}H_{15}N_3)_2,H_2Cr_2O_7$ and $(C_{17}H_{15}N_3)_4,(H_2Cr_2O_7)_3$, and the *platinochloride* of this base have been obtained.

Hydroxymethyldiphenylmetadiazine has been obtained by E. v. Meyer (*loc. cit.*); it is formed from the amido-compound by dissolving the latter in glacial acetic acid, and decomposing it with nitrous acid, or by heating it with dilute hydrochloric acid in a sealed tube at 180°; it melts at 250°, and dissolves in 1183·5 parts of absolute alcohol at 20°. The amido-compound dissolves in 51·3 parts of absolute alcohol at 20°.

Amidodiphenylmetadiazine (m. p. 120—121°) can be obtained when methyl cyanide (8·2 grams), phenyl cyanide (20·5 grams), and sodium (4·5 grams) are mixed together in a reflux apparatus, sealed from the air by mercury. It yields hydroxydiphenylmetadiazine (m. p. 281°, this vol., p. 68; Abstr., 1889, 1008) when heated with strong hydrochloric acid at 180° in a sealed tube.

The constitution of hydroxymethyldiphenylmetadiazine is settled by the fact that it can be obtained by the interaction of benzamidine hydrochloride, ethyl benzoylmethylacetate, and potassium hydroxide at 50—60°. By substituting acetamidine and propionamidine respectively for benzamidine, and allowing the reaction to go on for a long time, hydroxymethylphenylmethylmetadiazine (m. p. 175·5°) and hydroxymethylphenylethylmetadiazine (m. p. 180—181°) are obtained respectively. When a mixture of acetamidine and ethyl propionylpropionate is similarly treated with potassium hydroxide, hydroxymethylethylmethylmetadiazine (m. p. 167·5°, this vol., p. 68; Abstr., 1889, 685) is obtained; its constitution is thereby settled.

A. G. B.

Anilidopropionic Acid and α-Anilidobutyric Acid. By O. NASTVOGEL (*Ber.*, 23, 2009—2015; compare Abstr., 1889, 1012).—

α-Acetanilidopropionic acid, NAcPh·CHMe·COOH, is formed, together with the two isomeric diphenyl-αγ-dimethyl-βδ-diketopiperazines previously described (*loc. cit.*), when α-anilidopropionic acid is heated with acetic anhydride at 160—180° for two hours. It crystallises from hot water in prisms, and from benzene in plates, melts at 143°, and is readily soluble in most ordinary solvents, but only sparingly in cold benzene, carbon bisulphide, and cold water.

A compound which melts at 163°, and seems to have the composition $C_{20}H_{22}N_2O_2$, is obtained, together with diphenyl-αγ-diethyl-βδ-diketopiperazine (m. p. 260°), when α-anilidobutyric acid is heated with acetic anhydride; it crystallises in colourless needles, and is readily soluble in most ordinary solvents, except ether and hot water.

F. S. K.

Isomerism of the Diphenyl-αγ-dimethyl-βδ-diketopiperazines. By O. NASTVOGEL (*Ber.*, **23**, 2016—2022; compare preceding abstract).—An acid (m. p. 78—80°) of the composition $C_{18}H_{20}N_2O_3$, which is probably anilidopropionylanilidopropionic acid, is formed, together with resinous products and an acid melting at 96°, when diphenyl-αγ-dimethyl-βδ-diketopiperazine (m. p. 183·5°) is heated with potash. It melts at 78—80°, with partial decomposition, and is readily soluble in all solvents except water and light petroleum; when heated, it is converted principally into the piperazine (m. p. 144—146°). Diphenyl-αγ-dimethyl-βδ-diketopiperazine (m. p. 144—146°), when treated in like manner, yields the same acid, melting at 78—80°.

A crystalline acid melting above 90° is obtained when the fractions of low melting point, obtained in separating the two isomeric diphenyldimethyldiketopiperazines (Abstr., 1889, 1012), are boiled with potash; when this acid, or the acid melting at 96° (see above) is heated at 120°, it is converted into a third isomeric diphenyldimethyldiketopiperazine, which crystallises from dilute alcohol in prisms, and melts at 172—173°.

F. S. K.

Diphenyl-αγ-diethyl-βδ-diketopiperazines. By O. NASTVOGEL (*Ber.*, **23**, 2022—2025).—Diphenyldiethyldiketopiperazine (m. p. 145°) is formed when diphenyl-αγ-diethyl-βδ-diketopiperazine (m. p. 260°; compare Abstr., 1889, 1012) is boiled with alcoholic potash, and the mixture of acids thus obtained heated at 120°. It crystallises from dilute alcohol in long, colourless needles, melts at 145°, and is readily soluble in most ordinary solvents, but only moderately in hot light petroleum and hot ether, and very sparingly in hot water; when heated for a short time with alcoholic potash, it is reconverted into the isomeride (m. p. 260°).

F. S. K.

Diphenylketopiperazine and Diphenyl-αβ-diketopiperazine. By C. A. BISCHOFF and O. NASTVOGEL (*Ber.*, **23**, 2026—2030).—*Anilidoethylenephenylamidoacetic acid*,

NHPh·CH₂·CH₂·NPh·CH·COOH,

is formed when diphenylketopiperazine (Abstr., 1889, 1009) is boiled with alcoholic potash; it crystallises from a mixture of ether and light petroleum in colourless prisms, melts at 116° with decom-

position, and is reconverted into the piperazine by boiling alcohol, hot water, or cold dilute acids.

Diphenylnitrosoketopiperazine, $C_{16}H_{15}N_3O_2$, is obtained when diphenylketopiperazine is treated with sodium nitrite in glacial acetic acid solution; it is a yellow, amorphous powder, decomposes at 220—235°, and is readily soluble in glacial acetic acid, chloroform, aniline, and nitrobenzene, but only sparingly in benzene, xylene, and acetone, and insoluble in ether, alcohol, and light petroleum.

When diphenylketopiperazine is oxidised with chromic acid in cold glacial acetic acid solution, it is converted into diphenyl-$\alpha\beta$-diketopiperazine (Abstr., 1889, 1015); this diketo-derivative, on oxidation with chromic acid in acetic anhydride solution, is converted into tetraketopiperazine, and when treated with nitrous acid in concentrated sulphuric acid solution, it yields a yellow, crystalline compound, of the composition $C_{16}H_{10}N_6O_9$, which melts at 290°, and does not give Liebermann's reaction. Boiling potash decomposes diphenyl-$\alpha\beta$-diketopiperazine into ethylenediphenyldiamine and oxalic acid.

Diparethoxydiphenyldiketopiperazine,

$$OEt\cdot C_6H_4\cdot N<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CO\end{matrix}>N\cdot C_6H_4\cdot OEt,$$

prepared by heating ethylenediethoxydiphenyldiamine with chloracetic acid and sodium acetate at 140—150°, separates from alcoholic ether in almost colourless crystals, melts at 162°, and is readily soluble in hot benzene and hot alcohol, but only sparingly in ether.

F. S. K.

Action of Chloracetic Acid and Oxalic Acid on Ethylene-orthoditolyldiamine. By C. A. BISCHOFF and O. NASTVOGEL (*Ber.*, **23**, 2031—2035).—A *ditolylpiperazine*, melting at 153·5—154·5°, is obtained when ethyleneorthoditolyldiamine is heated with chloracetic acid and sodium acetate. It crystallises in slender needles, and is isomeric with the compound obtained from orthotoluidine and ethylene bromide (compare Bischoff, Abstr., 1889, 1010).

A colourless, crystalline compound, which has the composition of a *dichloracetylditolyldiamidoethane*,

$$CH_2Cl\cdot CO\cdot N(C_6H_4Me)\cdot CH_2\cdot CH_2\cdot N(C_6H_4Me)\cdot CO\cdot CH_2Cl,$$

is formed, when chloracetic chloride is added to a benzene solution of ethyleneditolyldiamine; it melts at 211—212°, and is readily soluble in alcohol, but only sparingly in cold water, and almost insoluble in ether.

Glycollic acid orthotoluidide, $C_6H_4Me\cdot NH\cdot CO\cdot CH_2\cdot OH$, is obtained when the preceding compound is heated with orthotoluidine and sodium acetate; it separates from alcohol in colourless crystals melting at 188—189°. When diorthotolyl-$\alpha\beta$-diketopiperazine is boiled with alcoholic potash, it is converted into a crystalline acid, which melts at about 100° with decomposition, and is very unstable, being reconverted into the diketopiperazine when it is kept over sulphuric acid; its *barium* salt, $(C_{18}H_{19}N_2O_3)_2Ba$, crystallises with 10 mols. H_2O.

F. S. K.

Action of Chloracetic Acid and Oxalic Acid on Ethyleneparaditolyl- and Ethylene-α-dinaphthyl-diamine. By C. A. BISCHOFF and O. NASTVOGEL (*Ber.*, **23**, 2035—2040).—Diparatolylketopiperazine (Abstr., 1890, 1009) is gradually decomposed by boiling alcoholic potash yielding an unstable acid, which is readily reconverted into the ketopiperazine; the *barium* salt of this acid has the composition $(C_{18}H_{22}N_2O_2)_2Ba + 4H_2O$. When diparatolylketopiperazine is treated with sodium nitrite in glacial acetic acid solution, it yields small quantities of a reddish, crystalline compound, which melts at 171—174°, and gives Liebermann's reaction, but the principal product is *diparatolyl-αβ-diketopiperazine*, $C_{18}H_{18}N_2O_2$. The last-named compound can also be obtained by oxidising diparatolylketopiperazine with chromic acid in glacial acetic acid solution; it crystallises from hot alcohol in colourless plates, melts at 263°, and is readily soluble in aniline, glacial acetic acid, acetone, chloroform, alcohol, concentrated nitric acid, and hydrochloric acid, but only sparingly in xylene, carbon bisulphide, ether, and hot water, and insoluble in cold water and light petroleum. On oxidation with chromic acid in acetic anhydride solution, it seems to be converted into diparatolyltetraketopiperazine, and when boiled with alcoholic potash, it is converted into ethyleneditolyldiamine, oxalic acid, and an acid which seems to have the constitution $C_6H_4Me\cdot NH\cdot CH_2\cdot CH_2\cdot N(C_6H_4Me)\cdot CO\cdot COOH$. This acid decomposes at 135°, but does not melt completely until the temperature rises to 197°, and its salts are not easily obtained in crystals: when boiled with glacial acetic acid, it is reconverted into diparatolyldiketopiperazine.

A green, crystalline substance, which seems to be *ethylenedinaphthyldiamine hydrochloride*, $C_{22}H_{20}N_2,HCl$, is obtained when ethylene-α-dinaphthyldiamine is heated at 165° for half an hour with chloracetic acid and sodium acetate; it melts at 221—223°, and is readily soluble in glacial acetic acid and aniline, but only sparingly in most other solvents. F. S. K.

Action of Acetic Anhydride on the Anilides, Toluidides, and Naphthalides of Malic Acid. By C. A. BISCHOFF and O. NASTVOGEL (*Ber.* **23**, 2040—2047).—A colourless, crystalline compound of the composition $C_{32}H_{28}N_4O_4$ is formed when malic dianilide (m. p. 197°, not 175° as stated by Arppe, *Annalen*, **96**, 106) is heated with acetic anhydride at 145—150°; it softens at 290°, melts at 300° with decomposition, and is only sparingly soluble in hot alcohol, but more readily in glacial acetic acid and concentrated sulphuric acid. It is possibly a mixture of two geometrically isomeric anilides of the acid described below.

Diphenyl-αγ-diketopiperazine-βδ-homocarboxylic acid,

$$COOH\cdot CH_2\cdot CH<^{NPh\cdot CO}_{CO\cdot NPh}>CH\cdot CH_2\cdot COOH,$$

is obtained, together with aniline and small quantities of a substance of low melting point, when the preceding compound is boiled with alcoholic potash; it separates from hot water in crystals, melts at 226—228°, and is readily soluble in alcohol, ether, glacial acetic acid,

and acetone, but only sparingly in benzene, chloroform, and light petroleum.

Malic acid orthotoluidide, $C_6H_4Me\cdot NH\cdot CO\cdot CH(OH)\cdot CH_2\cdot COOH$, is obtained when malic acid (1 mol.) is heated at 140—150° with orthotoluidine (2 mols.); it crystallises from alcohol in colourless needles, melts at 178°, and is soluble in hot water, but only sparingly in ether.

Orthotoluidine malate, $C_7H_9N,C_4H_6O_5$, is formed when the base is treated with malic acid in ethereal solution; it melts at 122—125°, and is soluble in water, alcohol, benzene, xylene, and acetone; when heated with acetic anhydride at 130—140°, it yields malic acid and acetotoluidide.

Malic diorthotoluidide, $C_6H_4Me\cdot NH\cdot CO\cdot CH(OH)\cdot CH_2\cdot CO\cdot NH\cdot C_6H_4Me$, is obtained, together with malic toluidide (see below), when orthotoluidine is melted with malic acid (1 mol.); it crystallises from alcohol in colourless plates, melts at 180·5—181·5°, and is readily soluble in alcohol, acetone, and glacial acetic acid, but only sparingly in chloroform, light petroleum, and ether; its solutions give an orange-red coloration with ferric chloride.

Malic orthotoluidide, $CO<\begin{matrix}N(C_7H_7)\cdot CO\\ CH(OH)\cdot CH_2\end{matrix}$, separates from a mixture of benzene and ether in crystals, melts at 114·5—116°, and is soluble in most ordinary solvents, but only sparingly in ether and light petroleum; its solutions give an orange-red coloration with ferric chloride.

Malic diparatoluidide, $C_{18}H_{20}N_2O_3$, prepared by heating paratoluidine with malic acid at 150—160°, crystallises from glacial acetic acid, melts at 205—208°, and is only sparingly soluble in benzene, acetone, and xylene, very sparingly in alcohol and ether, and insoluble in water, alkalis, chloroform, and light petroleum.

Fumaric diparatoluidide, $C_{18}H_{18}N_2O_2$, is formed when the preceding compound is heated with acetic anhydride at 160°. It crystallises in needles, turns brown at 289—292°, does not melt below 360°, and is insoluble in almost all ordinary solvents; when boiled with alcoholic potash, it yields fumaric acid.

Malic α-dinaphthalide, $C_{24}H_{20}N_2O_3$, prepared by heating malic acid (1 mol.) with α-naphthylamine (2 mols.) at 150—160°, separates from alcohol in crystals, melts at 205° and is readily soluble in glacial acetic acid, chloroform, benzene, aniline and ethylene bromide, but only sparingly in alcohol and insoluble in water, ether, alkalis, and acids; when heated with acetic anhydride, it yields a crystalline substance melting at 223—224°, which seems to be the acetyl-derivative, $C_{26}H_{22}N_2O_4$.

Malic β-dinaphthalide, $C_{24}H_{20}N_2O_3$, is formed, together with malic β-naphthalide, when malic acid is heated with β-naphthylamine; separates from aniline in crystals, melts at 260—263° with decomposition, and is almost insoluble in all ordinary solvents except aniline.

Malic β-naphthalide, $CO<\begin{matrix}N(C_{10}H_7)\cdot CO\\ CH(OH)\cdot CH_2\end{matrix}$, separates from hot water and alcohol in crystals, and melts at 193°. F. S. K.

Attempts to prepare Aromatic Tetra- and Tri-ketopiperazines. By C. A. BISCHOFF and O. NASTVOGEL (*Ber.*, **23**, 2051—2055).—The author's attempts to synthesise diphenyltetra- and diphenyltriketopiperazine were unsuccessful. Isoamyl oxanilate, prepared by treating isoamyl chloroxalate with aniline in ethereal solution, is decomposed on heating into oxanilide and isoamyl oxalate; when saturated with hydrogen chloride in the cold and then distilled, it yields oxanilide, carbonic anhydride, carbonic oxide, and isoamyl chloride.

When ethyl phenyloxamate is distilled, it is decomposed into alcohol, carbonic anhydride, carbonic oxide, oxanilide, and phenylcarbylamine; when treated with sodium ethoxide, it yields sodium oxanilate.

Diphenyl-$\alpha\gamma$-diketopiperazine and oxanilide are formed when phenylamidacetanilide is heated with oxalic acid at 140—145°, but the two compounds cannot easily be separated.

Monophenyloxamide (m. p. 224°) and chloracetanilide (m. p. 134·5°) are formed when chloracetamide is heated with oxanilide at 230°; the two products can be separated by treatment with light petroleum, in which chloracetanilide is readily soluble. F. S. K.

Attempts to prepare Closed Chains containing two Nitrogen-atoms and two, three, and six Carbon-atoms. By C. A. BISCHOFF and O. NASTVOGEL (*Ber.*, **23**, 2055—2060).—Methylene iodide and aniline react at 105—110° yielding a vitreous product which seems to consist of a mixture of the two compounds $CH_2(NHPh)_2$ and $NPh<\substack{CH_2\\CH_2}>NPh$.

Trimethylene bromide and aniline, in presence of sodium carbonate, combine together at 140° yielding a grey powder, the hydrochloride of which separates from hot alcohol in crystals, and melts at 221—224°.

Diphenylpiperazine (m. p. 163°) and aniline are obtained when ethylenediphenyldiamine is heated with succinic acid at 175—180°; when succinic anhydride is employed in place of the acid, diphenylpiperazine and a new crystalline acid are formed. This acid seems to have the constitution $NHPh\cdot CH_2\cdot CH_2\cdot NPh\cdot CO\cdot CH_2\cdot CH_2\cdot COOH$; it melts at 76—80° with decomposition, and forms a sparingly soluble barium salt.

Ethenyldiphenylamidine (m. p. 132°) is formed, together with some compounds which contain chlorine, when carbonyl chloride is passed into phenylamidacetanilide heated at 140°. F. S. K.

Derivatives of 1-Phenylpyrazole. By L. BALBIANO (*Ber.*, **23**, 1448—1453).—*Phenylpyrazoledicarboxylic acid* (1, 3, 5) is obtained when phenyldimethylpyrazole, prepared by treating acetylacetone with phenylhydrazine, is oxidised with an alkaline solution of potassium permanganate. It crystallises from alcohol in small, colourless plates, melts at 255—256° with decomposition, and is only very sparingly soluble in chloroform, benzene, warm light petroleum, and cold water, but more readily in ether and hot water. The *am-*

monium salt, $C_3N_2HPh(COONH_4)_2$, crystallises in plates, melts at 210—212° with decomposition, and is very readily soluble in water. The *lead* salt, $C_3N_2HPh(COO)_2Pb$, and the *silver* salt, $C_3N_2HPh(COOAg)_2$, are crystalline and almost insoluble in water. The *barium* salt is deliquescent.

Phenylbromopyrazoledicarboxylic acid (1, 4, 3, 5) prepared by treating the preceding compound with bromine (1 mol.) in cold glacial acetic acid solution, separates from hot dilute acetic acid in colourless, nodular crystals, melts at 244° with decomposition, and is only sparingly soluble in hot water, but more readily in warm alcohol and glacial acetic acid. The *ammonium* salt, $C_3N_2BrPh(COONH_4)_2$, crystallises in needles and melts at 190—192° with decomposition. The *lead* salt, $C_3N_2BrPh(COO)_2Pb$, is almost insoluble in boiling water. The *silver* salt is precipitated in a gelatinous condition, but becomes crystalline on boiling. The *barium* salt is deliquescent. When phenylbromopyrazoledicarboxylic acid is heated at 240—250°, it is converted into phenylbromopyrazole (1, 4), melting at 81°, identical with the bromo-derivative obtained by brominating 1-phenylpyrazole (this vol., 797).

Phenyldimethylbromopyrazole (1, 3, 5, 4) is formed when phenyldimethylpyrazole (1, 3, 5) is treated with bromine in glacial acetic acid solution. It is a yellow, pleasant smelling liquid, soluble in alcohol but insoluble in, and heavier than, water; when oxidised with potassium permanganate in alkaline solution, it is converted into phenylbromopyrazoledicarboxylic acid (m. p. 244°). F. S. K.

Diazothiazoles and their Decompositions. By A. HANTZSCH (*Ber.*, **23**, 1436—1478). The hydrate of ethyl diazomethylthiazolecarboxylate can be isolated in a solid condition by treating ethyl amidomethylthiazolecarboxylate in a suitable manner. This hydrate has probably the constitution $\begin{matrix} COOEt\cdot C\text{——}S \\ \Vert \\ CMe\cdot N \end{matrix}\!\!>\!C\cdot N{:}N\cdot OH$; the hydroxyl-group in this compound can be easily displaced by a halogen-atom. Analogous halogen-derivatives can be obtained in like manner from amidothiazole, and the compounds thus produced can be easily converted into thiazoles by reducing agents, and into hydroxy-thiazoles by treatment with alkalis.

When ethyl diazomethylthiazolecarboxylate is treated with alcohol, nitrous acid is eliminated, and a peculiar azimido-derivative is formed.

A full account of these experiments will be published in the *Annalen*. F. S. K.

Oxidation of Phenylmethyltriazolecarboxylic Acid. By J. A. BLADIN (*Ber.*, **23**, 1810—1815).—When the above acid is heated for several days on the water-bath with alkaline permanganate, the ring is not broken down, but the side chain is oxidised, and *phenyltriazoledicarboxylic acid*, $\begin{matrix} C(COOH){:}N \\ | \\ N{:}C(COOH) \end{matrix}\!\!>\!NPh$ is formed, and may be obtained

as a white, amorphous mass by cautiously adding hydrochloric acid and cooling the solution.

But if the solution is not kept cool, this compound rapidly loses carbonic anhydride, and *phenyltriazolecarboxylic acid*, $C_2N_3HPh\cdot COOH$, is obtained. This crystallises from water in brilliant plates which melt with decomposition at 184°, probably forming phenyltriazol. It dissolves easily in alcohol and acetic acid, sparingly in water, and hardly at all in benzene. The position of the carboxyl-group is not yet determined. The *alkali salts* are very soluble. The *silver salt*, $C_9H_6N_3O_2Ag + 1\frac{1}{2}H_2O$, forms a sparingly soluble, white, amorphous precipitate, easily convertible into fine needles. The *copper salt*, $(C_9H_6N_3O_2)_2Cu$, is a blue, insoluble, crystalline precipitate. The *hydrochloride*, $C_9H_7N_3O_2,HCl$, forms small plates. The *methyl salt*, $C_9H_6MeN_3O_2$, crystallises in small, colourless prisms melting at 116·5—117°, and soluble in alcohol and ether. The *ethyl salt*, $C_9H_6EtN_3O_2$, forms colourless prisms melting at 72°, very soluble in alcohol, ether, and benzole, but not in light petroleum. The amide,

$$Ph\cdot C_2N_3H\cdot CONH_2 + \tfrac{1}{2}H_2O,$$

forms asbestos-like needles melting at 194°, and dissolving in water and alcohol. C. F. B.

Ethoxycaffeïne. By H. THOMS (*Chem. Centr.*, 1890, i, 865; from *Pharm. Centralhalle*, **31**, 207—208).—Ethoxycaffeïne is prepared by dissolving bromocaffeïne in alcohol, introducing the necessary amount of sodium, and then boiling. It dissolves less readily in water than caffeïne, is readily soluble in hot alcohol, and melts at 138—138·5°. When boiled with hydrochloric acid, the ethyl-group is eliminated; by evaporating with chlorine, amalic acid is formed, which dissolves in ammonia with red colour. Ethoxycaffeïne differs from caffeïne in its behaviour towards alkalis; sodium or potassium hydroxide does not precipitate caffeïne, even when the solution is 1 gram in 10 grams of water, whilst ethoxycaffeïne is precipitated, although not quantitatively. For the identification of ethoxycaffeïne, the murexide test, its behaviour towards aqueous potash, and the melting point will serve. The author ascribes to it the formula

$$CO\begin{array}{l}\diagup NMe\cdot C(OEt)\colon C\cdot NMe \diagdown \\ \diagdown NMe \text{———} \overset{|}{C} \text{═══} N \diagup\end{array}O.$$

J. W. L.

Quinine, Cinchonidine, and their Isomerides. By O. HESSE (*Annalen*, **258**, 133—144).—Anhydrous quinine (quinine anhydride) which the author proposes to name "homoquinine," melts at 174·4—175°; the substance obtained by crystallising the trihydrate from alcohol or ether, and drying first in a desiccator and then at 120°, melts at 171·2—172°; the powder obtained by heating the compound $C_{20}H_{24}N_2O_2,C_6H_6$ at 120° melts at 171·6—172°.

Cinchonidine melts at 202·4°, homocinchonidine at 207·6°; the latter can be converted into the former by treatment with warm 25 per cent. sulphuric acid.

The melting points given above were very carefully determined in Roth's apparatus. F. S. K.

Conversion of Tropidine into Tropine. By A. LADENBURG (*Ber.*, **23**, 1780—1781).—When tropidine is treated with hydrobromic acid, a small quantity of a base is obtained which is not volatile with steam, and may thus be separated from tropidine. When distilled, it was found not to boil at a constant temperature; the distillate seemed still to contain bromine, which was removed by treatment with silver oxide. In this way a strong base was obtained, which, when treated with tropaic acid and hydrochloric acid, yielded a substance that reacted like atropine; the base was thus probably either tropine or metatropine.

The author still adheres to the formula $NMe{:}C_5H_7{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, but thinks it may possibly belong to metatropine, whilst tropine itself has the formula $NMe{:}C_5H_7{\cdot}CHMe{\cdot}OH$. C. F. B.

Alkyl-hydrastines and their Derivatives. By E. and F. SCHMIDT (*Arch. Pharm.* [3], **28**, 221—257).—The hydrastine employed was freed from its yellow colour by crystallisation from alcohol. *Hydrastine methiodide*, $C_{21}H_{21}NO_6,MeI$, formed by heating hydrastine with methyl iodide is obtained in tufts of prismatic or needle-shaped crystals, slightly soluble in water, more easily in alcohol. These crystals are anhydrous, sinter about 197°, and melt at 202° to 205°. By treating the aqueous solution with excess of silver chloride, hydrastine methochloride was produced, but could not be obtained in a crystalline state. The corresponding aurochloride, $C_{21}H_{21}NO_6,MeCl,AuCl_3$, was then formed by precipitation, and on recrystallisation from an acidified aqueous solution, appeared as fine, yellowish-red, anhydrous needles, melting at 183° to 184°. The platinochloride, also anhydrous, could only be obtained as an amorphous, yellow precipitate melting at 204° to 205°. *Hydrastine methylammonium hydroxide*, $C_{21}H_{21}NO_6,MeOH + H_2O$, is obtained by treating an aqueous solution of hydrastine methiodide with moist silver oxide. The compact, yellowish crystals become colourless when recrystallised from an aqueous solution, and melt at 214° to 215°. The compound when dissolved in boiling water, or heated at 100°, is converted into methylhydrastine hydroxide.

Methylhydrastine, $C_{21}H_{20}MeNO_6$, is obtained on treating a hot aqueous solution of hydrastine methiodide with normal potash. It is easily soluble in alcohol, ethyl acetate, and methyl alcohol, with splendid green fluorescence. Recrystallised from alcohol, it forms yellow needles showing green fluorescence, whilst the ethyl acetate solution yields beautiful, lustrous, compact, yellow needles, which are anhydrous and melt at 156° to 157°. *Methylhydrastine platinochloride*, $(C_{21}H_{20}MeNO_6)_2,H_2PtCl_6 + 2H_2O$, is obtained as a yellow, flocculent precipitate, which melts at 199° to 200°. The water found was a little higher than is indicated by the formula. The aurochloride, $(C_{21}H_{20}MeNO_6)_2,HAuCl_4$, formed as a dirty-yellow, flocculent precipitate, recrystallised from dilute acidified alcohol as brownish-red needles melting at 205° to 206°. *Methylhydrastine hydrogen sulphate*, $C_{21}H_{20}MeNO_6,H_2SO_4$, occurs as a yellow, crystalline powder, when the base is dissolved in absolute alcohol and sulphuric acid diluted with alcohol is added. The normal sulphate, $(C_{21}H_{20}MeNO_6)_2,H_2SO_4$, is formed when the base is dissolved

in the least possible amount of dilute sulphuric acid. On evaporating the solution to dryness and crystallising from hot alcohol, beautiful, yellow laminæ are obtained which in alcohol show a fine, green fluorescence. *Methylhydrastine hydrochloride*, $C_{21}H_{20}MeNO_6,HCl + H_2O$, is obtained, like the sulphate, as slender, yellow needles, easily soluble in water, somewhat difficultly soluble in alcohol with green fluorescence, melting at 233° to 234°. The corresponding *nitrate*, $C_{21}H_{20}MeNO_6,HNO_3$, was similarly obtained. The salts of methylhydrastine are yellow, and their solutions are strongly fluorescent, whilst hydrastine salts as described by Kerstein (this vol., p. 648—649) are colourless, and exhibit little or no fluorescence. *Methylhydrastine methiodide*, $C_{21}H_{20}MeNO_6,MeI$, results from the action of methyl iodide on the base. Recrystallised from dilute alcohol, it forms well-shaped, greenish-yellow, prismatic crystals melting at 250° to 251°. From this reaction it is inferred that methylhydrastine, like hydrastine, is a tertiary base. Methylhydrastine is partially oxidised by sulphuric acid and manganese dioxide, only hemipinic acid and a volatile base being detected among the products. Oxidation with nitric acid is also somewhat incomplete; the chief product is again hemipinic acid with probably dimethylamine, carbonic anhydride, and oxalic acid. Methylhydrastine methiodide, when acted on by potassium hydrate, yields trimethylamine and a non-nitrogenous compound, $C_{20}H_{18}O_7$, which occurs as small, colourless, four-sided plates melting at 168° to 169°. This compound, when oxidised by potassium permanganate, yields hemipinic acid and an acid which has not yet been fully examined.

Methylhydrastine alcoholate, $C_{21}H_{20}MeNO_6,EtOH$, is obtained in minute, light-yellow crystals, when methylhydrastine is dissolved in alcohol, water added until turbidity appears, the precipitate redissolved by heating, and the solution finally allowed to cool. The crystals melt at 95° to 96°, so that the compound analysed was only dried at 90°. Their aqueous and alcoholic solutions exhibit only a relatively slight fluorescence. The platinochloride,

$$[C_{21}H_{20}MeNO_6,EtOH]_2,H_2PtCl_6,$$

is obtained as a light-yellow powder melting at 163° to 164°. When methylhydrastine alcoholate is dissolved in as little alcohol as possible, and excess of nitric acid is added, a little methylhydrastine nitrate (?) separates as a yellow, crystalline powder; on adding ether to the filtrate, almost colourless, needle-shaped crystals of methylhydrastine alcoholate nitrate, $C_{21}H_{20}MeNO_6,EtOH,HNO_3$, gradually form, which melt at 145° to 146°. Corresponding hydrochlorides and sulphates were obtained. The alcoholate, heated with sulphuric or hydrochloric acid, is decomposed yielding the salt of methylhydrastine. The mother liquor from methylhydrastine alcoholate completely loses its green fluorescence on evaporation, and yields drusy groups of small, brownish crystals on cooling, which become colourless when recrystallised from dilute alcohol. *Methylhydrastine hydroxide*, $C_{21}H_{22}MeNO_7 + 2H_2O$, thus formed melts at 151° to 152°, and dissolves in alcohol without fluorescence. Of the three mols. H_2O contained in this base, one enters directly into the molecule; the other two are combined as

water of crystallisation. The production of this compound from hydrastine methylammonium hydroxide has already been mentioned; the same product is obtained by dissolving methylhydrastine in boiling water and allowing the solution to cool. The hydroxide evaporated with sulphuric or hydrochloric acid gives a salt of methylhydrastine. *Methylhydrastine hydroxide platinochloride*,

$$(C_{21}H_{22}MeNO_7)_2,H_2PtCl_6,$$

is obtained by dissolving the hydroxide in acidified water and precipitating in the cold with platinic chloride. The yellow, amorphous flocks become crystalline after a time. The yellow, crystalline powder melts at 208°. *Methylhydrastine hydroxide hydrochloride*,

$$C_{21}H_{22}MeNO_7,HCl,$$

is prepared by dissolving the base in absolute alcohol, adding excess of fuming hydrochloric acid, and then ether; on dissolving it in alcohol and reprecipitating by ether, small, colourless needles are obtained which melt at 182° to 183°. A corresponding sulphate can be similarly prepared, and other salts of the same base. Methyl iodide produces a greenish, resinous mass with the base; the chloride, formed by dissolving this compound in alcohol and treating with silver chloride, is a similar resinous mass. The chloride dissolved in water and precipitated with platinum chloride gives a yellow, flocculent platinochloride, $[C_{21}H_{22}MeNO_7,MeCl]_2PtCl_4$. This composition confirms the supposition that 1 mol. of water in the base is more intimately combined than the other two. *Ethylhydrastine hydroxide*, $C_{21}H_{22}EtNO_7 + 2H_2O$, prepared from ethylhydrastine, like the corresponding methyl compound, forms colourless needles which, heated in a capillary tube, melt at 130°, but solidify to a yellow mass at a somewhat higher temperature, and then melt again at 206—207°. As in the case of the methyl compound, 2 of the 3 mols. of water contained in the ethyl hydroxide are easily removed over sulphuric acid, whilst the third mol. is more intimately combined—as the composition of the platinochloride also shows. By evaporation with dilute mineral acids, the colourless ethylhydrastine hydroxide becomes converted into the yellow, strongly fluorescent hydrastine salt. Ethylhydrastine hydroxide platinochloride, $[C_{21}H_{22}EtNO_7]_2,H_2PtCl_6 + 4H_2O$, was obtained as a yellow, flocculent precipitate which melts at 137° to 138°. Owing to the close relationship existing between hydrastine and narcotine, the former containing two methyl-groups, and the latter three similar groups, it is probable that narcotine, or one of its isomerides, may be prepared from hydrastine. This investigation is still in progress. J. T.

Lobeline. By H. PASCHKIS and A. SMITA (*Monatsh.*, **11**, 131—132). —In order to extract the alkaloïd from *Lobelia inflata*, the plant was exhausted with dilute acetic acid, and the filtered extract made alkaline and exhausted with ether. On evaporating the ethereal solution, the alkaloïd remained as a viscid, honey-yellow mass having an odour resembling that of honey and tobacco. The alkaloïd was purified by dissolving it in ether, shaking the ether with an

excess of water containing hydrochloric acid, treating this with an alkali, and again exhausting with ether. After repeating this process three times, the ethereal solution was dried with potash, and the ether distilled off in an atmosphere of hydrogen.

When lobeline (1 gram) is suspended in a solution of 10 per cent. potash (300—400 c.c.) and treated with 4 per cent. potassium permanganate, added in small quantities, until the greenish colour of the solution only disappears after remaining some time, benzoic acid is formed. G. T. M.

Ptomaïnes. By O. DE CONINCK (*Compt. rend.*, **110**, 1339—1341).—The ptomaïne $C_{10}H_{15}N$ (Abstr., 1888, 730) is a yellowish, viscous liquid with an agreeable odour; it is heavier than, and only slightly soluble in water, but dissolves readily in ether, absolute alcohol, acetone, and light petroleum. After being dried over fused potash, it boils at about 230° with partial decomposition. It oxidises rapidly in presence of oxygen or air, becomes brown, and forms a thick resin soluble in acids. The *hydrochloride* is obtained by saturating the base with hydrochloric acid and concentrating rapidly in a vacuum. It forms yellowish needles which are highly deliquescent and very soluble in water. In presence of a very small quantity of air, the crystals acquire a rose colour, and with larger quantities of air they become brown and form a resinous product identical with that obtained by direct oxidation of the base. The *platinochloride* is a deep-red solid insoluble in cold water, very soluble in warm water, and decomposed by boiling water. It is permanent in dry air, but in moist air loses hydrogen chloride, and is partially oxidised. C. H. B.

Physiological Chemistry.

Respiration in the Horse during Rest and Work. By N. ZUNTZ and C. LEHMANN (*J. Physiol.*, **11**, 396—398).—The authors defend their method of experimentation recently criticised by F. Smith (this vol., p. 392), and in turn pass unfavourable remarks on the methods adopted by Smith. According to them the chief fallacies of Smith's method consist in using a mask of too great capacity, and in determining the amount of gaseous interchange immediately after instead of during work. Their own values are in general far greater than those of Smith's, and they compare the two sets of results in the following table:—

		Litres per minute.			Resp. quot.
		Air expired.	CO_2 expired.	O_2 absorbed.	
Rest..	S	35	0·534	0·772	0·69
	L and Z. Respiration through a mask	69	1·570	1·722	0·92
	L and Z. Respiration through a cannula in the trachea	44	1·478	1·601	0·92
Walk. .	S	63	0·509	0·962	0·53
	L and Z	177	4·342	4·766	0·90
Trot..	S	136	1·835	3·056	0·59
	L and Z	333	7·516	8·093	0·93

W. D. H.

Absorption of Fat. By O. Minkowski (*Practitioner*, **45**, 139—140; from *Berlin klin. Wochensch*, 1890, No. 13).—From an examination of the fæces, it was found that after extirpation of the pancreas the fat of the food is no longer absorbed. An exception to this was milk, whose fatty constituents were more or less taken up. If the fresh pancreas of the pig were mixed with the food, then the greater part of the fat was absorbed. To the view that the pancreatic juice breaks up fat into fatty acid and glycerol. the results lend no support; on the contrary, although the pancreas was altogether absent, the fatty matter in the fæces was for the most part found split up; this likewise renders untenable the theory that fat is largely absorbed in the form of soaps. That the action of the juice is not a special one upon the absorbent elements of the intestine is evident from the fatty matter of milk being ingested in the absence of the gland, and this also shows that what is important is the form in which the fat comes into contact with the intestinal mucous membrane. Milk is a fine emulsion, differing much from the saponified emulsion of alkaline carbonates. Bernard showed that whilst ordinary alkaline emulsions are destroyed by acidulation, the fat running into large drops, a pancreatic emulsion remains unchanged by this treatment; the same property is possessed by the emulsified fat of the chyle and of milk. Kühne suggested that the fat globules of a pancreatic emulsion possess an albuminous membrane which facilitates their adhesion to the protoplasm of the epithelial cells of the intestine. This, however, is questionable.

The further observation was made that an action of the pancreas on fatty matters takes place, although there is no direct flow of the pancreatic secretion into the intestinal canal, provided a part of the pancreatic tissue capable of performing its functions remains in the organism. Thus, after partial extirpation of the gland, fat absorption, though impaired, was not altogether prevented.

The fact is also established, that in dogs complete removal of the pancreas leads to diabetes; and Hirschfeld has shown that in diabetic

patients the absorption of proteïd and fat is much impaired. This is perhaps an indication that the cause of diabetes in some cases is disease of the pancreas. W. D. H.

Destruction of Glucose by Blood and Chyle. By R. LEPINE and BARRAL (*Compt. rend.*, **110**, 1314—1316).—The authors have made further experiments, which confirm the existence in the blood, and especially in the chyle, of a ferment which destroys glucose (this vol., p. 810). This ferment disappears in cases of acute diabetes. The action of the ferment is greatly accelerated by rise of temperature, but is retarded by the presence of carbonic anhydride. The destructive action exerted by living tissues is much greater in presence of this ferment than when it is absent. All the experiments were made with a dog. The authors term the ferment the *glycolytic* ferment. C. H. B.

Cattle Marrow. By K. THÜMMEL (*Arch. Pharm.*, **228**, 280—290).—Fresh marrow contains 7·62 per cent. water, and 0·39 to 0·48 per cent. membrane; its melting point varies from 37° to 46°, and solidifying point varies from 30° to 38°, depending on the varying amounts of trioleïn present, which may be 43 to 62·9 per cent., as deduced from the iodine number for various samples. Hehner's number, which gives the percentage of insoluble fixed fatty acid in the fat, is 93·4 for old animals, and 93 for young ones. Köttstorf's saponifying process gives 191·3 alkali for young cattle, and 204·7 for old cattle, per 1000 of glyceride. The corresponding numbers are, according to Benedikt, for tallow, 196·5; olive oil, 191·8 to 203; and butter, 227. The amount of glycerol, calculated from the foregoing, is for old cattle 10·56 per cent., and for young ones 11·18. The fatty acids were found to consist approximately of oleic, 40 per cent.; stearic, 35; and palmitinic, 25. In the marrow of young cattle, the oleïc acid amounts to 60 per cent. Volatile fatty acids are present in small quantity only. Medullic acid, described by Eylert as existing in marrow, could not be found. J. T.

Pigments of the Peridinia. By F. SCHÜTT (*Chem. Centr.*, 1890, 1, 767—768; *Ber. deut. bot. Gess.*, **8**, 9—32).—The pigment of a large number of sea-water *Peridinia* becomes separated at their death into two pigments, the one of which is red, soluble in water, and diffuses itself therein, whilst the other is yellowish-green and remains in the chromatophores. The former has been named "phykopyrrin" by the author, and is obtained in concentrated solution by extracting the *Peridinia* with a little water. If this brownish-red solution is treated with alcohol, no change is perceptible; if shaken with benzene, the pigment passes into the latter, but appears to suffer change thereby, the extract having a yellow colour.

The extracted peridinia are next boiled with water, and eventually all the soluble pigment passes into solution, leaving the peridinia greenish-yellow coloured. The extract obtained with boiling water is yellowish-brown, and has not the same appearance as that obtained with cold water. The author names that obtained with

cold water α-phykopyrrin, and that obtained by boiling water β-phykopyrrin. Both pigments seem to have the same physical properties.

If the peridinia, after extraction with cold and hot water, are treated with successive portions of alcohol, extracts varying in colour from port-wine-red to chlorophyll-green are obtained, which the author names peridinin- and peridinia-chlorophyllin.

The physical properties of these several pigments are—

(1.) *Phykopyrrin*, brownish-red in aqueous solution, yellow in alcohol, ether, benzene, carbon bisulphide, and glacial acetic acid. It has a strong absorption band in the red λ 65—68, corresponding with the chlorophyll band I, and another at λ 60—62, corresponding with the chlorophyll band II. *Peridinin*, insoluble in water, readily soluble in alcohol, benzene, ether, carbon bisulphide, glacial acetic acid, little soluble in light petroleum. Weak absorption band in the orange λ 64. *Peridinia-chlorophyllin*, insoluble in water, soluble in alcohol, ether, benzene, carbon bisulphide, glacial acetic acid; little soluble in light petroleum. It shows a strong absorption band in the red, corresponding with the chlorophyll band I, and a minor band in the green. J. W. L.

Pathological Effusions. By W. D. Halliburton (*Brit. Med. Journ.*, 2, 1890, 193—196).—In this research, analyses were made of a number of dropsical effusions into the serous sacs. The word serous used in this connection is an unfortunate one, as the fluid in them is not serum, but very nearly resembles plasma in its composition. The proteïds present are fibrinogen, serum-globulin, and serum-albumin, and the analyses chiefly relate to the quantities of these which are present. They illustrate the following points:—

1. That when simultaneous dropsies occur in various parts, those in the pleura, pericardium, and peritoneum have, so far as the amount of their albuminous constituents is concerned, different compositions, and are all much richer in proteïd matter than the fluid of subcutaneous œdema. This is probably due to the varying conditions of vascular pressure in the different situations.

2. That in successive tappings the fluid removed from a serous sac remains remarkably constant in composition.

3. That the total proteïd, the yield of fibrin, and the specific gravity are all much higher in exudations, that is, inflammatory effusions, than in transudations, that is, simple effusions due to derangements of vascular pressure. This may be illustrated by the following table of average results of analyses of fluid removed from the pleural cavity:—

	Specific gravity.	Total proteïd per cent.	Fibrin per cent.
From cases of inflammation (pleurisy)	1021	4·5903	0·0173
From cases of simple dropsy (hydrothorax)	1014	1·7748	0·0086

4. That in cases of simple dropsy, the fluid obtained from cases of heart disease is richer in total proteïds than in that due to liver or kidney disease. This may be illustrated by the following table:—

	Average percentage of proteïds in acetic fluid.
Cases of liver disease	1·760
Cases of kidney disease................	2·209
_a_e_ of heart disease	4·589

This appears to confirm a view urged by Wooldridge (*Proc. Roy. Soc.*, **45**, 309), that in heart disease there is also a change in the blood which leads to increased exudation through the vascular walls.

5. That the proteïd quotient (that is, relation of albumin to globulin) varies considerably, but the variations show no fixed relation to the cause of the effusion. The proteïd quotient of effusions varies directly as that of the blood (Salvioli, *Du Bois Reymond's Archiv*, 1881, 269; F. Hoffman, *Arch. exp. Path. Pharm.*, **16**, 133; Pigeaud, *Maly's Jahresb.*, **16**, 474), and observations are still wanting to enable us to state under what conditions the proteïd quotient of the blood rises and falls. This is of some interest, for seemingly diffusion through living membranes differs from that through dead membranes; in the latter case globulin diffuses more slowly than albumin (Gottwalt, *Zeit. physiol. Chem.*, **4**, 423).

6. That aqueous humour resembles the so-called serous effusion in its composition and reactions.

Analyses of pericardial, hydrocele, and œdema fluids are given, but present no points of particular interest. Peptones and albumoses are absent in all these fluids, so differing from cerebro-spinal fluid, (Abstr., 1887, 514; 1889, 793). In those cases where a reducing substance is present, it appears to be sugar; this is another point in which serous effusions differ from cerebro-spinal fluid.

The analysis of one specimen of ovarian fluid showed that in addition to the ordinary proteïds, true mucin was present. Pseudo-mucin or paralbumin, which often occurs in ovarian fluid, was absent.

W. D. H.

Proteïds in Urine. By D. Noel Paton (*Brit. Med. Journ.*, **2**, 1890, 196—201).—It was Senator (*Virchow's Arch.*, **60**, 476) who first stated that in all cases of albuminuria both of the chief proteids of the blood-plasma (serum-globulin and serum-albumin) are present. The proteïd quotient (that is, the ratio of albumin to globulin) may, however, vary within wide limits; in the present observations between 0·6 and 39. In acute nephritis, when blood is absent, the quotient is high. When hæmoglobin is present, the globulin is of course in excess. As the disease becomes more chronic, the quotient sinks. This alteration depends probably on the condition of the patient, and is probably related to a similar change in the blood-plasma. Waxy degeneration of the kidneys cannot be distinguished from the ordinary forms of nephritis by the high proportion of serum-globulin as was formerly maintained by Senator; Maguire's suggestion (*Lancet*, **1**,

1886, 1062), that functional albuminuria is characterised by a high proportion of serum-globulin, is also incorrect. In every case the quotient varies much in the course of the day, the proportion of globulin being always highest in the night; its greatest fall is after breakfast, and in most cases it rises again in the evening. Milk diet, as observed by Lecorché and Telamon (*Traité de l'Albuminurie*, Paris, 1888), has a peculiar effect in increasing the proportion of serum-albumin. The amount of proteïds passed appears to bear a direct proportion to the amount of proteïds ingested, and, excluding milk diet, the increase of the proteïds in the urine on a diet rich in those substances, appears to be chiefly due to an increase in the serum-albumin. The variation in the proportion of the albumin to the globulin in the urine is frequently so great that it can hardly be believed that it is connected with a similar change in the plasma. The experiments performed would, however, suggest that a high pressure favours the transudation of serum-albumin, whilst a low pressure increases the proportion of serum-globulin transuded.

W. D. H.

Action of Rennin and Fibrin-ferment. By A. S. LEA and W. L. DICKINSON (*J. Physiol.*, **11**, 307—311).—The term *rennin* is suggested in place of that of rennet-ferment. Fick (*Pflüger's Arch.*, **45**, 293) has recently stated that the mode of action of the clotting ferments is fundamentally different from that of the ordinary digestive enzymes, inasmuch as the molecules of the former do not require to come into close relationship with the molecules of the substance acted on, but that when once the change has been set up by the ferment in any one portion of the substance, this change is propagated from particle to particle without the further necessary intervention of the ferment. In the present experiments, measured quantities of milk were introduced into tubes of different sizes, and warmed to 40°. Rennin solution, also warmed to 40°, was then placed in the bottom of the tubes by means of a long pipette with capillary ending, so as to form a clear layer beneath the milk. The tubes were then kept at 40°. In about 20 minutes a clot at the junction of the two fluids had formed; the supernatant milk was completely fluid, and remained so for from five hours in the narrow tubes to seven hours in the wider ones. Control tubes, in which the rennin was mixed with the milk, showed complete coagulation in three minutes. Precisely similar results were obtained with fibrin-ferment solution and dilute salted plasma. The ultimate coagulation that occurs is explicable on the ground that there is a gradual dissemination of the ferment by convection currents. This view is supported by the fact that the final clotting occurs sooner in the narrow than in the wide tubes; in the latter case, convection currents would not be so active.

Milk placed in a porous battery cell, the cell being immersed in a beaker of rennin solution, did not clot for over 24 hours, when the observation was suspended.

From these experiments the conclusion is drawn that Fick is in error, and that the mode of action of the clotting ferments is essentially similar to that of other well-characterised enzymes, as far

as contact between the ferment and the alterable substance is concerned.
W. D. H.

Influence of Salts on Clotting. By S. RINGER and H. SAINSBURY (*J. Physiol.*, **11**, 369—383).—Previous experiments have shown that minute quantities of various salts of the alkalis and alkaline earths, such as occur normally in the blood, have very distinct actions on the contraction of the heart-muscle and voluntary muscle. Some favour, others hinder, the contraction, and the two sets of salts are antagonistic to one another. The formation of myosin, causing *rigor mortis* in dead muscle, is a process completely analogous to the formation of fibrin in dead blood, and both are similar in many respects to the formation of caseïn in milk by the activity of rennet. Hermann's view of the phenomena of muscular contraction is, that it is essentially the same thing as the death of a muscle, the difference being one of degree only. Dead muscle and contracted muscle are similar in electrical potential, and in the fact that they have an acid reaction due to sarcolactic acid. The formation of a clot of myosin during contraction has, however, never been proved, and in the present research it was thought that the question might be further elucidated by a study of the action of various salts on the coagulation process (in blood, milk, and pathological effusions); it was found that these salts act as favouring or hindering agents on the act of coagulation, precisely in the same way as they do on the contraction of muscle. The main result of the research is therefore that the experiments afford a confirmation of Hermann's theory that contraction and coagulation are analogous phenomena.

The individual conclusions respecting the salts investigated are as follows:—

Calcium is an essential to the act of clotting. This was previously shown by Green (Abstr., 1888, 306) to be true for calcium sulphate and blood clotting. Hammarsten long ago pointed out the necessity of calcium phosphate for the efficient action of rennet, and Freund (*Centr. Med. Wiss.*, Oct., 1889) believes this salt plays also an important part in fibrin-formation. In the present research the chloride was found to be a very efficient salt in favouring coagulation, and the opinion is expressed that the effect of calcium is a generic effect belonging to all its salts. Strontium and barium act like calcium, but are less powerful. The action of all three metals is largely controlled by the solubilities of their salts. Potassium and sodium salts, on the other hand, have a restraining influence on coagulation, the latter metal being the more powerful in this direction. There is antagonism between the salts of the alkaline earths on the one hand, and those of the alkaline metals on the other.
W. D. H.

Osmosis with Living and Dead Membranes. By E. W. REID (*Journ. Physiol.*, **11**, 312—351).—A full account, with diagrams, tracings, and figures of apparatus used, of experiments of which a preliminary account has already appeared (this vol., p. 277).
W. D. H.

Pernicious Anæmia. By F. W. Mott (*Practitioner*, **45**, 81—93).—The case published is similar in essential points to two already described (Abstr., 1888, 1324, and this vol., p. 1017). The present case is remarkable as occurring in a young subject (æt. 11 years), in the fact that the urine, though loaded with uric acid crystals, was not highly coloured, and in the presence of more iron in the spleen than has been previously noted. The following table gives the amount of iron found in various organs:—

Organ.	Wt. in grams.	Total iron as ferric oxide.
Liver	900	1·33 grams.
Spleen	100	0·17 ,,
Pancreas	50	0·01 ,,
Kidneys	100	0·01 ,,

In connection with Delépine's work (see next abstract), it is suggested that pernicious anæmia is an exaggeration of a normal physiological process. When the absorption of the products of digestion occurs, the blood is replenished by new materials, and plethora would occur if there were not a proportional destruction of the plasma and corpuscles to form urea and pigments which leave the body by the natural channels. Whether the excessive destruction that occurs in pernicious anæmia is due to a poison, the result of bacterial activity derived from the alimentary canal, must for the present be considered unproved, for it does not seem that there is always a relation between the pyrexia, the anæmia, and the colour of the urine. Moreover, severe putrefactive processes may occur in the intestine without any pernicious anæmia being brought about.

It is known that peptone has a very marked influence upon the blood, and it is possible to suppose that this substance, if not reconverted into albumin during absorption, might be the poison in question. The liver and spleen of a dog, into whose circulation peptone solution had been injected, yielded the iron reaction very markedly; but this may have been accidental, and further experiments are promised on this subject. W. D. H.

Normal Storage of Iron in the Liver. By S. Delépine (*Practitioner*, **45**, 94—98).—Pigment is constantly found in liver cells and in some of the endothelial cells of the intralobular capillaries; it may be particulate, or diffused through the cell in a state of solution. It gives the reactions of ferric salts, and these are more intense between 8 and 12 hours after food, and reach a minimum immediately after the ingestion of food. The pigment is, as a rule, most abundant in the portal zone. The liver has thus a ferrogenic function, which probably consists of a separation of iron from effete iron-containing pigment, a storage of that iron in the form of a loose compound, and the gradual formation of a more stable albumino-ferruginous compound analogous if not identical with hæmoglobin, and ready for assimilation by the young red blood-corpuscles. Pernicious anæmia is probably an exaggeration of this normal process.

W. D. H.

Physiological Action of Morphine and its Derivatives. By R. STOCKMAN and D. B. DOTT (*Brit. Med. Journ.*, **2**, 1896, 189—192).—A medium dose of morphine first depresses the spinal cord, and this is followed by tetanus. When a minimum narcotic dose is given, the narcosis is not deep, and no tetanic symptoms follow. When the dose is sufficient to produce both sets of symptoms, the morphine is slowly absorbed, and only a small portion reaches the cord at first; hence the depression; as more is absorbed, more comes into contact with the nerve cells, and then tetanus occurs. Tetanus can, however, be induced at once without any preliminary depression if the morphine be thrown directly into the circulation so as to reach the cord in sufficient quantity. The usual sequence of depression and stimulation is thus entirely a matter of dosage.

Methylmorphine, ethylmorphine, and amylmorphine have identical physiological actions, the narcotic action of morphine being diminished and its tetanic action increased.

Acetyl-, diacetyl-, benzoyl-, and dibenzoyl-morphine have a much greater depressant action in small doses on the cord and on the respiratory centre than morphine; their narcotic action is not nearly so profound. Increase of dose, instead of deepening the narcosis, brings on tetanic symptoms which are much more marked than those produced by morphine.

Morphine Sulphuric Ether and Nitrosomorphine.—In these two substances, the introduction of the radicles HSO_3 and NO modifies the action of morphine much in the same way as the introduction of alcoholic and other acid radicles.

Methylmorphium Chloride and Methylcodeïum Sulphate.—From experiments with these two additive products, the conclusion is drawn that the actions of morphine or of codeïne are not very profoundly altered by the chemical change. The paralysing action on the motor nerves is considerably increased, and the narcotic action is lessened.

Chlorine-derivatives (chlorocodide and trichloromorphine) have the characteristic actions of the morphine-group on the central nervous system. In addition, they act energetically as muscle poisons, soon destroying the contractile power of the voluntary muscles with which they first come in contact at the place of injection, and more gradually affecting the other muscles of the body. Chlorine is well known to be a powerful muscle poison.

Methocodeïne.—In this substance, two methyl molecules are introduced into morphine, one replacing a hydroxyl hydrogen-atom, whilst the other is introduced into the body of the morphine molecule, $C_{17}H_{17}MeNO(OH)\cdot OMe$. Here the distinguishing features of morphine poisoning are wholly absent, the chief symptom observed being gradual poisoning of the voluntary muscles.

The experiments carried out in this research were performed ou frogs and rabbits.

W. D. H.

Physiological Action of Pituri and Nicotine. By J. N. LANGLEY and W. L. DICKINSON (*Jour. Physiol.*, 11, 265—306).—Pituri is an alkaloïd extracted from the leaves of a shrub (*Duboisia Hopwoodii*) which grows in Australia. The Australian blacks make with

the leaves a quid for chewing. The main result of the present experiments is to show that the physiological action of pituri is identical with that of nicotine. It is possible that pituri leaves, like tobacco leaves, may contain more than one alkaloïd, but that pituri leaves contain nicotine does not admit of doubt unless it be supposed that different chemical substances have the same physiological action.

The bulk of the paper is taken up with a very complete account of the physiological action of the two drugs on both frogs and mammals. A complete bibliography of the subject is also given.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Preparation of Wine Yeasts. By A. ROMMIER (*Compt. rend.*, **110**, 1341—1343).—In order to obtain pure wine yeast, the juice of carefully selected grapes is allowed to ferment, and small quantities of the fermented liquid are added to filtered and sterilised grape juice. A number of successive cultivations in grape juice are then made with intervals of one to four days, and the final cultivations are made in a solution of sugar mixed with the necessary inorganic salts. In this way the less energetic yeasts are eliminated, and only *Saccharomyces ellipsoideus* remains. C. H. B.

Alcoholic Fermentation and Conversion of Alcohol into Aldehyde by Champignons du Muguet. By G. LINOSSIER and G. ROUX (*Compt. rend.*, **110**, 868—870).—Existing statements as to the fermentative power of champignons du muguet (the fungus of the lily of the valley) are very contradictory. The authors find that when carefully sterilised liquids are inoculated with a pure cultivation of the fungus with all the usual precautions, quantities of alcohol were obtained varying from 2·7 per cent. in the case of a sugar solution containing inorganic salts, to 5·5 per cent. in the case of wort from dried raisins. The fungus ferments levulose and maltose as well as glucose. It develops at the expense of saccharose, but neither inverts it nor ferments it. It cannot assimilate lactose. In a mixture of levulose and dextrose, both sugars are attacked, but the latter disappears the more rapidly. In addition to alcohol, glycerol, succinic acid, a notable quantity of acetic acid, a little butyric acid, and a somewhat large quantity of aldehyde are formed. A small quantity of the aldehyde may be a product of excretion of the ferment, but the greater part is formed by the oxidation of alcohol in presence of air and under the influence of the ferment. The ferment, in fact, develops readily in very dilute alcohol mixed with inorganic salts, a mixture of aldehyde and acetic acid being formed. The acetic acid, on the other hand, is probably formed by the direct oxidation of the aldehyde by the oxygen of the air, without intervention of any life process. The ferment, in fact, cannot develop at the expense of aldehyde even in presence of suitable salts.

This is the first instance in which aldehyde has been found to be

the chief product of fermentation by a low organism. The general behaviour of champignons du muguet, the maximum quantity of alcohol produced, the rate of fermentation, &c., show that it is more nearly related to the *Mucorinæ* than to *Saccharomyces*, and this result agrees with the authors' deduction on morphological grounds that this fungus did not belong to the group of *Saccharomyces*.

C. H. B.

The "Bouquet" of Fermented Liquids. By G. JACQUEMIN (*Compt. rend.*, **110**, 1140—1142).—The characteristic bouquets of wines from various districts are due to the special characters of the yeast used in each district. One and the same must fermented with the yeast obtained from several different districts gave wines having the bouquet characteristic of the district from which the particular yeast producing them had come. Even in a 10 per cent. solution of sugar, the cultivated yeasts, although producing very little alcohol, will develop their characteristic bouquet in a very remarkable and intensified degree.

C. H. B.

The Nitrifying Organism. By WINOGRADSKI (*Ann. Agron.*, **16**, 273—274; from *Ann. de l'Institut Pasteur*, **4**, 213, 261).—After trying several nutritive media, the author found that the organic matter generally introduced is prejudicial to nitrification, and he therefore employed river water (Lake of Zurich) with the addition of 1 gram per litre each of ammonium sulphate and potassium phosphate. A little magnesium or calcium carbonate is added, and the liquid sterilised by ebullition and then fertilised with a few drops from a previous operation. Five organisms were recognised in the light surface deposit formed on the liquid, but these had no nitrifying power. The body of the liquid is generally perfectly clear, but when the nitrification is very active the liquid becomes slightly clouded about the fifth or sixth day by oval, slightly fusiform organisms, moving with great agility. These disappear after some time, but the layer of magnesium or calcium carbonate at the bottom becomes entangled in a gelatinous, greyish deposit of thick groups of a fine, oval bacterium. It is impossible to grow this bacterium on the gelatin plates commonly used, and the author takes advantage of this fact to isolate it. Some drops of the deposit are removed by a capillary tube and placed in a flask of sterilised water, and drops of this attenuated liquid are cultivated on separate plates of gelatin; after some days, the plates are examined, and those showing no growths are selected as containing the nitrifying organism alone. Fragments of these sown in the ammoniacal liquid employed give rise to nitrates in measurable quantities. The author goes on to infer that as the nitrifying bacterium lives, develops, and carries out its functions in a medium containing minerals only, it must derive the carbon necessary to its structure from the carbonic anhydride of carbonates, the energy necessary to reduce the carbonic anhydride being derived from the heat disengaged by the oxidation of ammonia into nitric acid. It, therefore, furnishes us with an example of a non-chlorophyllous cell able to effect the decomposition of carbonic anhydride.

J. M. H. M.

Note by Abstractor.—On March 13, 1890, Dr. P. F. and Mrs. Frankland communicated to the Royal Society an account, with drawings, of the nitrifying bacillo-coccus, isolated by a process of dilution, and refusing to grow in gelatin peptone. Warington, commenting (*Chem. News*, **61**, 135) on their experiments and his own, remarks that "the medium they made use of was an ammoniacal solution containing no organic matter." He also appears to have isolated the same organism from cultures in "weak solutions of ammonium salts containing the necessary nutritive salts but no organic matter." In connection with this point in the investigations of Frankland, Warington, and Winogradski, I may be permitted to point out that in a paper published in this Journal (Trans., 1886, 632—681), and afterwards translated in full in the *Ann. Agronom.*, I showed that "the merest traces of organic matter," if any, "such as may be furnished accidentally by occasional exposure to the dust of the air, are sufficient for complete nitrous fermentation of the quantities of ammonia used in these experiments" (*loc. cit.*, p. 654), and that in general "the presence of a tartrate or any similar organic body is distinctly prejudicial to nitrification" (p. 654). On this account, I adopted boiled well or river water with added ammoniacal salt as a suitable nitrifying medium, and remarked (p. 667), "In the purest well waters, there is a very slight flocculent deposit during nitrification; there is more deposit in the rapidly nitrifying waters. Nitrification in filtered well water, or in boiled well water seeded with a nitrifying solution free from fermentable organic matter, would probably furnish a deposit well suited for microscopic observation of the nitrifying organism, called by Schloësing and Muntz *Micrococcus nitrificans*" (p. 667). Using a solution almost identical with that since adopted by Winogradski, namely, plain water with the addition of an ammoniacal salt and a little potassium phosphate (p. 680), I also succeeded in suppressing the so-called incubating period of the nitrifying organism, and starting nitrification in a fresh solution in less than seven hours. But Winogradski's inference as to the decomposition of carbonic anhydride by this organism appears to me open to grave doubt.

J. M. H. M.

Action of Light on Acetic Fermentation. By M. GIUNTI (*Bied. Centr.*, **19**, 490—491; from *Staz. Sper. Agr. Ital.*, **18**, 171—183). —White wine was diluted with water, treated with acetic acid, sterilised, and inoculated with *Mycoderma aceti*, which had been cultivated in the same wine diluted. The liquid contained alcohol (4·51 vols. per cent.) and acetic acid (3·03 grams per litre). Two series of experiments were made under equal conditions, except that one was exposed to light, and the other kept in the dark, whilst a third experiment was made without the organism, the object of which was to correct errors in reading the volumes of gas. After three or four weeks the solutions were analysed. The results showed that direct sunlight hinders the development of the *Mycoderma aceti*, and consequently the acetic fermentation; even diffused daylight hinders the development if the surface of the liquid is not shaded. Prolonged sunlight did not, however, sterilise the liquid inoculated with *Myco-*

derma, but it might be possible to hinder the formation of acid in wines in this way. N. H. M.

Elaboration of Nitrates in the Plant. By O. LOEW (*Ann. Agron.*, **16**, 279—280).—On heating 3 grams of glucose and 1 gram of potassium nitrate at 60—70° for six hours with 200 c.c. of water and 110 grams of spongy platinum, 45·6 per cent. of the nitrogen was found transformed into ammonia, which was combined with acids formed by oxidation of the glucose. A rancid odour resembling caproic acid, valerian root, or rancid butter was at the same time developed. The author believes the vegetable cell may exercise a similar "catalytic" reducing action on nitrates previous to the elaboration of the nitrogen into protoplasmic compounds.

J. M. H. M.

Calcium Oxalate Crystals. By G. ACQUA (*Ann. Agron.*, **16**, 275). —The raphides so common in *Phytolacca dioica* are most numerous in the neighbourhood of the young shoots. There are no crystals in the embryo, but soon after germination they appear in the root cap, afterwards in the cotyledons; before their formation, the cells in which they are to appear are filled with gelatinous contents. If the young plants are grown in a nutritive solution containing no calcium, fresh crystals do not appear, but those already formed do not dissolve. Oxalic acid is formed in all the turgescent cells of the bark and pith; it unites with potash, and passes in solution through the intercellular spaces; in certain cells, distinguished by the nature of their contents, the calcium salts everywhere present precipitate the oxalate. Similar observations were made with *Mesembryanthemum acinaciforme* and *Euonymus japonicus*. The oxalate always remains where it is formed.

J. M. H. M.

Importance of Chlorine in the Plant. By C. ASCHOFF (*Ann. Agron.*, **16**, 275—277).—Knop concluded from his water-culture experiments that chlorine is not essential to the growth of plants; Beyer, Leydhecker, Nobbe, Siegert, and Wagner hold the contrary opinion. The author has experimented with common haricots, Spanish haricots, and maize, growing them in a nutritive solution containing magnesium sulphate, 0·1002 gram; potassium chloride, 0·1215 gram; calcium nitrate, 0·2674 gram; potassium phosphate, 0·1019 gram; and a trace of ferric chloride, per litre; also in the same solution, with the potassium chloride omitted and the ferric chloride replaced by ferric pyrophosphate; and in pure water. In the pure water, no growth took place; in the complete solution, the growth was normal, and the plants flowered and seeded, whether the cotyledons were removed from the seeds or not; in the solution deprived of chlorine, growth soon stopped, the roots aborted, the terminal buds dried up, and the leaves fell. The Spanish haricots when deprived of chlorine formed no tannin, but the common haricot did in both solutions. Chlorine may be considered necessary to the three plants experimented with. J. M. H. M.

Solanidine in Potato Shoots. By JORISSEN and GROSJEAN (*Ann. Agron.*, **16** 284—285).—The shoots thrown out by potato

tubers kept in the dark contain solanidine, which can be extracted by ether, treated with potash to remove oily matter, and purified by crystallisation from alcohol; 1·5 grams was obtained from 1 kilo. of the fresh shoots containing 90 per cent. of water. On analysis, the formula $C_{26}H_{41}NO_2$ was obtained. J. M. H. M.

Nitrogenous Constituents of the Tubercles of Stachys tuberifera. By A. v. PLANTA (*Ber.*, 23, 1699—1700).—In addition to stachyose (this vol., p. 1088), various nitrogenous compounds also occur in the tubercles of *Stachys tuberifera.* Of these, glutamine and tyrosine have been identified, and a base has also been obtained which is precipitated by phosphotungstic acid, and forms a hydrochloride and aurochloride somewhat resembling those of betaïne. Its exact nature has not yet been determined. H. G. C.

Yields and Composition of a Variety of Red Clover. By P. BAESSLER (*Bied. Centr.*, 19, 478—479).—The experiments were made with a Norwegian variety of red clover ("Totenklee"), distinguished by its hardiness and its producing large crops, in a humous, sandy soil containing, nitrogen, 0·2; lime, 1·2; potash, 0·1; phosphoric acid, 0·3 per cent. The manuring was superphosphate and sodium nitrate, and half of the experimented land had besides a top-dressing of a bye-product from the manufacture of potassium salts, containing about 50 per cent. of gypsum, 28 per cent. of calcium carbonate, 5 per cent. of lime, and 7·5 per cent. of potassium sulphate. The first crop gave, per acre, 132 cwt. of green fodder and 42·7 cwt. of hay without, and 168 cwt. of green fodder and 53·5 cwt. of hay with, the top-dressing of calcium and potassium salts.

The following numbers show the mean percentage composition of the air-dried hay of the two plots:—

Water.	Ash.	Crude fat.	Crude proteïn.	Crude fibre.	Non-nitrogenous extract.
14·55	6·33	2·09	14·00	22·40	40·63

Nitrogen.	Albuminoïd nitrogen.	Nitrogen as amides, &c.
2·24	1·84	0·40

The differences in composition of the produce from the two plots were only slight. N. H. M.

Decomposition of Rocks and Formation of Arable Soils. By A. MUNTZ (*Compt. rend.*, 110, 1370—1372).—A summary of the causes which are active in producing the disintegration of rocks. The author lays special stress on the importance of the part played by the nitric ferment and other low organisms (compare Abstr., 1887, 1135).

C. H. B.

Decomposition of Organic Manures in Soils. By A. MUNTZ (*Compt. rend.*, 110, 1206—1209).—In soils in which, from their nature (*e.g.*, acid soils), nitrification cannot take place, the nitrogen of the organic matter is converted into ammonia. In strong clay soils also

the nitrogen is almost completely converted into ammonia, very little nitrification taking place. The same result is observed with nitrifiable soils in which the nitric ferment has been killed by exposure to a temperature of 90°. Even with arable soils in which nitrification takes place rapidly, part of the organic nitrogen is converted into ammonia. If the soil has been heated to 120°, the formation of ammonia is, as a rule, prevented, but takes place if a small quantity of non-sterilised soil is added.

It follows from these results that the ammonia ferment exists in soils simultaneously with the nitric ferment, and produces a preparatory change, which is useful, if not essential, in the process of nitrification, and which accelerates the conversion of organic nitrogen into nitrates. C. H. B.

Green Manures as Suppliers of Nitrogen. By A. Muntz (*Compt. rend.*, **110**, 972—975).—Soil was mixed with green manure (lupin), dried blood, and ammonium sulphate respectively in such quantity that the proportion of nitrogen was 1 gram per kilo. The first soil, I, was light, and contained 2 per cent. of calcium carbonate; the second, II, was a strong, clay soil, containing but little lime; the time in both cases was three months, and the figures give the quantity of nitric nitrogen in milligrams per kilo.

	Green manure.	Dried blood.	Ammonium sulphate.
I..........	183	161	268
II..........	88	3·6	5·1

The relatively rapid nitrification with the bulky green manure in II is due to its effect in making the soil more pervious to the air.

An experimental plot at Vincennes was divided into four parts, which were treated with different manures, so that 100 kilos. of nitrogen was present per hectare. Eighteen days after spreading the manures, the milligrams of nitric nitrogen per kilo. were as follow:—

Green manure (lucerne).	Dried blood.	Ammonium sulphate.	No manure.
86·0	72·2	121·4	14·5

The weight of the crop of maize, cut in September, was as follows:—With green manure, 78,000 kilos.; with dried blood, 71,500 kilos.; with ammonium sulphate, 66,000 kilos.; with sodium nitrate, 78,500 kilos.; and with no manure, 39,500 kilos.

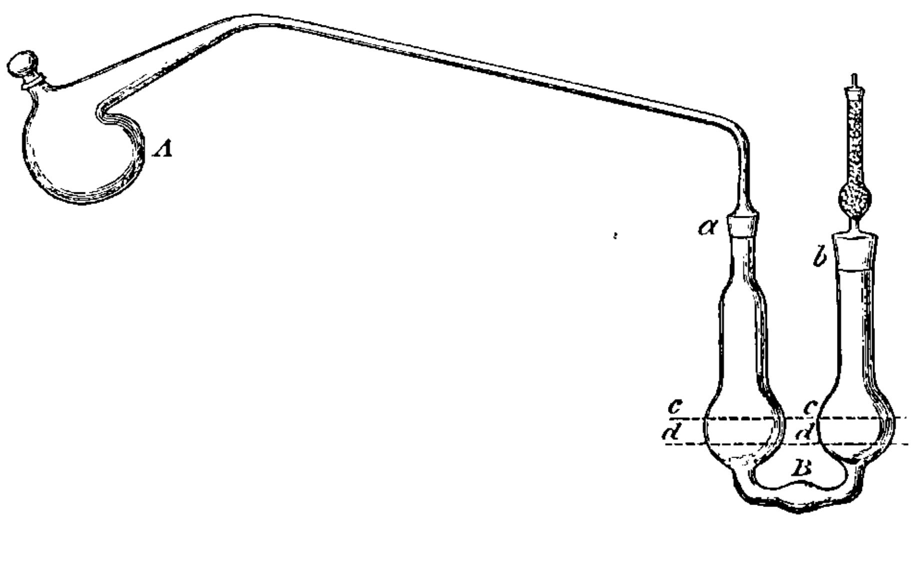
It follows that the efficiency of green manures is due to the ease with which their proteïd constituents are nitrified, and to the favourable influence which the manure exerts on the physical properties of the soil. C. H. B.

Analytical Chemistry.

Apparatus for Drying Substances under Diminished Pressure. By D. SIDERSKY (*Zeit. anal. Chem.*, **29**, 280—282).—The apparatus is essentially a water-oven, with a door which can be closed air-tight, and stop-cock connections by which the interior chamber can be exhausted by an air-pump, or refilled with dry air. In form it is a double-walled cylinder of copper, of about 30 cm. high and 26 cm. diameter, with conical ends; the annular space is filled with water which is kept boiling. Owing to the reduced pressure in the interior, substances dry with great rapidity, and with less tendency to decompose than in an ordinary water-oven. M. J. S.

Characteristic Reaction of Hydrogen Peroxide. By G. DENIGÈS (*Compt. rend.*, **110**, 1007).—A 10 per cent. aqueous solution of ammonium molybdate, mixed with its own volume of strong sulphuric acid, gives with a few drops of hydrogen peroxide a deep-yellow coloration. When more water is added, the intensity of the colour decreases more rapidly than the degree of dilution increases; but it is not affected by heating the liquid. The reaction will detect 0·0001 gram of hydrogen peroxide. A permolybdic acid seems to be formed; sodium molybdate may be used instead of the ammonium salt. C. H. B.

Estimation of Iodine. By W. STORTENBEKER (*Zeit. anal. Chem.*, **29**, 272—280; see Abstr., 1889, 185).—For processes involving the distillation of iodine, the author, whilst fully endorsing the statements of Topf (*Zeit. anal. Chem.*, **26**, 277), suggests the subjoined apparatus as simpler. The retort A has a capacity of 250 c.c.; the neck is 40 cm. long, and serves as a condenser; it is connected at *a* with the U-tube by grinding, and the joint is wetted (Topf, however,



states that ground joints are to be avoided, as iodine adheres with peculiar tenacity to ground surfaces). The U-tube is filled to *dd* with potassium iodide solution, with which also the beads in the small tube are moistened. It is plunged into cold water up to the level *cc*. The joint *b* may be of caoutchouc. No stream of gas is required, the steam being sufficient for the complete expulsion of the iodine. M. J. S.

Estimation of Iodine in Haloïd Salts. By F. A. GOOCH and P. E. BROWNING (*Amer. J. Sci.* [3], **39**, 188—201).—The method proposed consists in boiling the solution of the iodide with sulphuric and arsenic acids; the iodide is oxidised by the latter, and arsenious acid is formed, together with free iodine, which volatilises with the steam. The arsenious acid in the residual solution is titrated with standard iodine. There must be at least 25 per cent. by volume of strong sulphuric acid in the solution when the boiling is finished. The presence of considerable quantities of chlorides makes the result too low, owing to volatilisation of arsenious chloride; bromides are slightly oxidised by arsenic acid, and consequently make the result too high. It was found that in the case of the solutions experimented with, these errors might be corrected; the correction to be applied to the weight of iodine found being (weight of sodium chloride × weight of potassium iodide × 0·004) — (weight of potassium bromide × 0·0016).

The mode of proceeding in the analysis of a mixture of alkaline chlorides, bromides, and iodides may be summarised as follows:—

The substance (which should not contain more chloride than corresponds with 0·5 gram of sodium chloride, or of bromide more than corresponds with 0·5 gram of potassium bromide, or of iodide much more than the equivalent of 0·5 gram of potassium iodide) is dissolved in water in an Erlenmeyer beaker of 300 c.c. capacity, and to the solution are added 2 grams of dihydrogen potassium arsenate dissolved in water, 20 c.c. of a mixture of sulphuric acid and water in equal volumes, and enough water to increase the total volume to 100 c.c., or a little more. A platinum spiral is introduced, a trap, made of a straight two-bulb drying-tube, cut off short, is hung with the larger end downwards in the neck of the flask, and the liquid is boiled until the level reaches the mark put upon the flask to indicate a volume of 35 c.c. Great care should be taken not to press the concentration beyond this point on account of the double danger of losing arsenious chloride and setting up reduction of the arsenate by the bromide. On the other hand, although 35 c.c. is the ideal volume to be attained, failure to concentrate below 40 c.c. introduces no appreciable error. The liquid remaining is cooled and nearly neutralised with sodium hydroxide (ammonia is not equally good), neutralisation is completed by hydrogen potassium carbonate, an excess of 20 c.c. of the saturated solution of the latter is added, and the arsenious acid in solution is titrated by standard iodine in the presence of starch.

With ordinary care, the method is rapid, trustworthy, and easily executed, and the error is small. In analyses requiring extreme

accuracy, all but accidental errors may be eliminated from the results by applying the corrections indicated. C. F. B.

New Method of Estimating Sulphur in Inorganic Sulphides. By P. JANNASCH (*J. pr. Chem.* [2], **41**, 566—574).—The author has improved the absorption apparatus which he uses for his method of determining sulphur in inorganic sulphides by combustion in oxygen (compare Abstr., 1889, 1244). Instead of cylinders with corks, to which he objects as being likely to retain splashings in their pores, he now uses cylinders with glass stoppers which have tubes sealed through them. The tube which dips under the liquid in the first cylinder is widened at the top to admit of a cork through which the drawn-out and downward-bent end of the combustion-tube is thrust. The tube which does not dip under the liquid in the second cylinder is bent twice at right angles, and its other end dips into bromine-water in an Erlenmeyer flask. The operation is conducted as previously described (*loc. cit.*). When it is concluded (after about $\frac{3}{4}$ hour), all the absorbent is transferred to a beaker, strong hydrochloric acid (1 c.c.) added, and heated until all bromine is expelled; the sulphuric acid is then precipitated as barium sulphate, with all the usual precautions.

The author gives examples of analyses of blende, copper pyrites, and antimonite by this method, for which he claims rapidity, accuracy, and freedom from interference by other substances.

A. G. B.

Estimation of Arsenic by Marsh's Method. By B. KÜHN and O. SAEGER (*Ber.*, **23**, 1798—1803).—About 150 grams of pure zinc (sufficient for the decomposition of about 0·11 gram of arsenious acid) is placed in an Erlenmeyer flask, which is also provided with an india-rubber stopper through which pass a funnel, 50 cm. long, reaching to the bottom of the flask, and a delivery-tube bent at right angles. The latter is connected to a wash-bottle containing 50 c.c. of a 5 per cent. lead acetate solution, this to a drying-tube containing at least 100 grams of calcium chloride, and this, finally, to the shorter drawn-out end of the combustion-tube. The latter is made of hard glass tubing, of 10—12 mm. internal diameter; 80 cm. of it lie in a combustion-furnace, heated by 24 burners, and it is drawn out at both ends to a tube of about 5 mm. internal diameter for a length of 25 cm. at one end and 60 cm. at the other. Over the funnel, above mentioned, are two burettes, one containing the arsenic solution, the other dilute sulphuric acid (1 part by vol. of acid (sp. gr. 1·84) to 3 of water). The combustion-tube is heated to a dull-red heat, and sulphuric acid run into the flask, so as to sweep out the apparatus with a current of hydrogen. The acid is then arranged so as to drop in at about $\frac{3}{4}$ c.c. per minute, 25 c.c. of the arsenic solution is run in at about $\frac{1}{2}$ c.c. per minute, and the shorter, contracted limb of the combustion-tube is heated at three separate places with bunsen burners; if any arsenic is deposited here, it is a sign that the current of hydrogen is too slow. The current must not be so fast that the bubbles in the lead acetate bottle cannot be counted, and in order to see that no arsenic has escaped, a wash-bottle containing a little

silver nitrate should be connected with the further end of the combustion-tube. The arsenic is deposited as a mirror in the longer limb of the combustion-tube; it is brought as much as possible into one part of this by warming it, and sending a reversed current of hydrogen through if necessary. The piece of tubing is cut off, weighed, the arsenic dissolved in strong nitric acid, and the tube weighed again. Or if, as may happen in toxicological cases, it is desired to preserve the arsenic, the little piece of tubing should be placed inside a larger piece, drawn out at one end, and the arsenic sublimed into this end in a current of hydrogen. More than 0·1 gram of arsenic cannot be easily estimated, and, in any case, the results are not very exact, but the method is expeditious, and, for some purposes, may be useful.

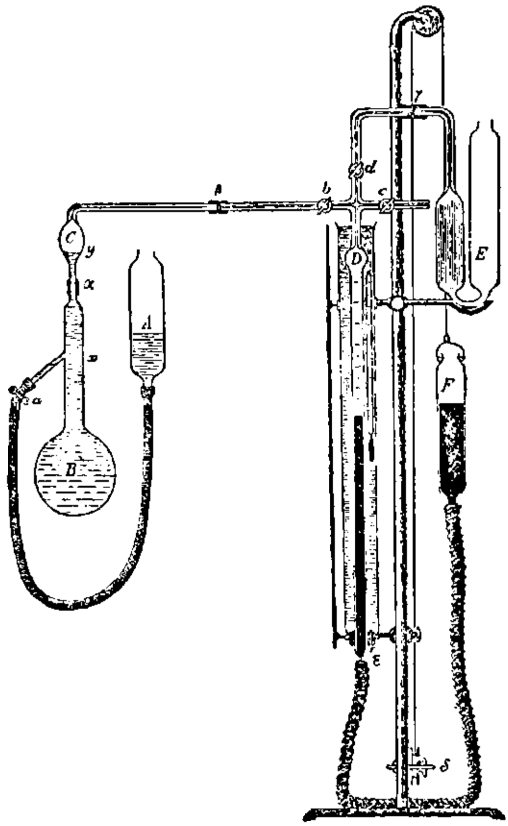
It has also been found that, contrary to the statement of the textbooks, arseniuretted hydrogen is decomposed to a considerable extent when it is passed over solid caustic potash, though not so easily as antimoniuretted hydrogen. C. F. B.

Estimation of Moisture and Carbonic Anhydride in Air. By J. S. HALDANE and M. S. PEMBREY (*Phil. Mag.* [5], **29**, 306—331).—The authors have improved the absorption method for determining the amount of water-vapour in the atmosphere. The absorption apparatus employed by them consists of a pair of test-tubes, 4 × 1 inch, filled with pumice soaked in sulphuric acid, and connected up in the ordinary way with well paraffined corks and glass tubing. When charged, the pair weighs about 80 grams. A counterpoise, in every respect similar to this apparatus, and exposed to the same conditions, should always be used to diminish the error in weighing. Experiment showed that air could be aspirated through such absorption-tubes at the rate of 7 litres a minute without appreciable quantities of moisture (less than 0·1 per cent.) escaping. A comparison with the psychrometric method showed errors in the latter ranging from +30 to −7 per cent.

The apparatus for absorbing carbonic anhydride was formed of another such pair of tubes, the first containing soda-lime, and the second pumice and sulphuric acid. The air must be perfectly dry before reaching the soda-lime tube, so that a simultaneous determination of moisture and carbonic anhydride was usually made, the rate of aspiration being in general 1 litre per minute. Here again the mean error is only about 0·1 per cent. Pettenkofer's method gave results 8 to 27 per cent. higher than those obtained by direct weighing. J. W.

Estimation of Carbonic Anhydride. By O. PETTERSSON (*Ber.*, **23**, 1402—1406).—The carbonic anhydride in all solid or liquid substances can be estimated by means of the following apparatus, which is more especially suitable for the determination of the gas when in a dissolved or partially combined state, as, for example, in natural spring or sea water. The substance containing the carbonic anhydride is boiled with dilute acid in the flask B under reduced pressure, and a slow stream of hydrogen, obtained from a small piece of iron or aluminium wire enclosed in a long capillary tube, intro-

duced into B, is passed through the liquid during the operation; in this way the whole of the carbonic anhydride is expelled, and bumping is avoided. If nitric acid has to be employed (compare this vol., p. 1027), the necessary quantity of hydrogen is obtained from a piece of aluminium wire, bound round with platinum wire.



The evolved gases are measured over mercury in a moist condition in the burette D, the carbonic anhydride being then absorbed with potash in the Orsat's tube E; the residual air can then be expelled through *c*, either partially or entirely, and the space C above the liquid exhausted at will, so that the boiling always takes place under greatly reduced pressure. The horizontal tube in connection with C is capillary; the others are narrow, but not capillary. As a rule, a small quantity (0·3—0·5 c.c.) of water collects on the surface of the mercury in D; this is removed, before the boiling is completed, by opening *b* and raising F.

The details of the operation are as follow:—The liquid to be analysed is introduced into B up to the mark *x*, the metal wire is thrown in, and the bulb-shaped tube C is securely connected at *α* with B and at *β* with the horizontal tube of the burette by means of india-rubber tubing. A sufficient quantity of dilute hydrochloric acid, or nitric acid, is then poured into A, the cocks *a* and *b* are opened (*c* and *d* being closed), and F is lowered by turning the roller *δ*; when the acid has risen to *y*, *a* is closed, and C is exhausted.

The stopcock *b* is then shut, F is raised until the level of the mercury in D and F is the same, and *d* is opened; a few large bubbles of air are then blown into *e* to equalise the temperature of the water in the tube surrounding D, and the level of the soda in E is brought to the mark on the capillary tube. The volume of the air in D, the temperature, and the barometric pressure are noted, and the air is then passed into E; after about two minutes, it is brought back into the burette, and its volume again measured. The air which remains in D, after exhausting, contains very little carbonic anhydride, and, except when the liquid in B is very rich in this gas, the quantity does not exceed 0·03 cm.

Before commencing to heat the liquid in B, the volume of air in D is reduced to about 13 c.c. by opening *c* and raising F; about half the residual air is then passed into E, *d* is closed, and F is lowered until the pressure in D is reduced to about 110—130 mm. On heating the liquid in B (by means of a rose-burner) and opening *b*, ebullition quickly commences, and the evolved gas collects in D without carrying over any appreciable quantity of water; small drops, which collect in the capillary tube, can be driven back into C by quickly raising F, and, in order to further prevent water from distilling over, the stopcock *b* can be kept closed, except when transferring the liberated gas to D. As soon as the burette is filled with gas, under a pressure of one-sixth to one-seventh of an atmosphere, *b* is closed, and the carbonic anhydride in the gaseous mixture is determined as before, the bunsen flame being meanwhile simply lowered. As a rule, this operation must be repeated two or three times in order to expel the whole of the carbonic anhydride; but, when after 10—15 minutes boiling only 0·02—0·03 c.c. of the gas is obtained, the boiling can be discontinued.

Quantitative experiments gave very good results. In estimating the carbonic anhydride in solid substances, the quantity of this gas present in the distilled water used must be determined separately.

The above diagram shows the apparatus one-twelfth its actual size.

F. S. K.

Valuation of Zinc-dust. By G. KLEMP (*Zeit. anal. Chem.*, **29**, 253—266).—The methods of Fresenius (Abstr., 1879, 400), Beilstein and Jawein (1880, 826), Barnes (1887, 80), and Morse (1885, 1012) depend on the treatment of the zinc with an acid and estimation of the hydrogen evolved: that of Drewsen (*Zeit. anal. Chem.*, **19**, 50), on the reducing action of the zinc on acidified potassium chromate. Topf (Abstr., 1887, 997) adds the zinc-dust to an excess of iodine and estimates the iodine left uncombined. Weil (Abstr., 1887, **301**, 1000) treats the zinc-dust with a known quantity of cupric chloride, and titrates the excess by stannous chloride. The results of Drewsen's method are irregular, and also low, compared with those of Topf and Fresenius. On the other hand, in the methods involving treatment with an acid, iron, and to some extent lead, which are often present as impurities, are estimated as zinc, although they are valueless when the zinc is used for reductions in alkaline solution, which is frequently the case. On this account, the author prefers to estimate the metallic zinc by its reducing action on potassium iodate

in alkaline solution. In concentrated solutions, containing a sufficient excess of iodate, zinc reduces the iodate to iodide, without any evolution of hydrogen, and on the subsequent addition of an acid, the iodide reacts with the excess of iodate setting free iodine in the proportion of 0·7799 part of iodine for 1 part of zinc (there are misprints in the numbers in the original). The iodine can now be distilled out, condensed in potassium iodide, and titrated with thiosulphate. The conditions for success are as follows:—There must be a certain excess of iodate and alkali, and the liquids should be as concentrated as is possible without precipitation of the iodate by the alkali. The zinc-dust must be very intimately mixed with the liquid, but it must not be wetted with water before adding the reagent.

For each 0·1 gram of zinc there should be used 0·1525 gram of potassium iodate in 3 c.c., and 3 grams of sodium hydroxide or 3·7 grams of potassium hydroxide in 10 c.c. The zinc (0·5—1 gram) is weighed into a dry stoppered bottle of about 200 c.c. capacity, some glass beads are added, and then the two reagents, previously mixed, and the bottle is vigorously shaken for five minutes. Warming is unnecessary. The contents of the bottle are now made up to 250 or 500 c.c. and 100 c.c. taken for distillation. The apparatus of Topf (*loc. cit.*) is the most convenient for the purpose. The condensing tubes may contain about 4 grams of iodide in 20 c.c. The liquid placed in the retort is acidified with dilute sulphuric acid, a slow stream of carbonic anhydride is passed through, and the contents of the retort are boiled until colourless. The iodine is then titrated with a thiosulphate solution containing about 7 grams per litre. Finely divided lead treated as above reduces iodate corresponding with about 3 per cent. of zinc, but when lead is mixed with zinc it slightly lowers the results. Iron has a similar effect, in consequence of the escape of a little hydrogen when the mixture is treated with the alkaline iodate. M. J. S.

Volumetric Estimation of Zinc. By L. BLUM (*Zeit. anal. Chem.*, **29**, 271—272).—Donath and Hattensaur have published (*Chem. Zeit.*, 1890, 323) a method for the titration of zinc in presence of iron in an ammoniacal tartrate solution by potassium ferrocyanide, the end being ascertained by mixing a drop with acetic acid. In presence of manganese, a frequent impurity in zinc ores, the results are too high, so that in most cases the method is useless. M. J. S.

Estimation of Zinc in its Ores. By D. CODA (*Zeit. anal. Chem.*, **29**, 266—271).—In the ordinary method, after removal of copper, &c., by hydrogen sulphide, the iron is precipitated from the hydrochloric acid solution by a mixture of ammonia and ammonium carbonate, and the zinc in the filtrate is titrated by sodium sulphide. The iron precipitate always carries down with it a portion of the zinc, which cannot be completely detached either by long standing, by boiling, or by a second precipitation. But in a sulphuric acid solution, containing ammonium sulphate, the latter salt adheres to the ferric precipitate in place of the zinc, and the whole of the zinc is obtained in the filtrate.

About 2·5 grams of the zinc ore is dissolved in 15—20 c.c. of nitro-hydrochloric acid and the solution evaporated to dryness; 15—20 c.c. of sulphuric acid is then added, and the whole heated until fumes of sulphuric acid escape. If metals precipitable by hydrogen sulphide are present, they must be removed, and the filtrate boiled to expel hydrogen sulphide. The filtrate is neutralised with ammonia, and then 40 c.c. more ammonia, containing one-fourth of ammonium carbonate, is added. The cooled mixture is made up to 500 c.c. and filtered, and 100 c.c. is taken for titration. The standard solution used is a 2 per cent. solution of crystallised sodium sulphide, the strength of which must be ascertained by an experiment with a quantity of pure zinc approximately equal to that in half a gram of the ore. This quantity is dissolved in 4 c.c. of hydrochloric acid, diluted, and made alkaline with 20 c.c. of ammonia. Each liquid is then diluted to about 250 c.c., and the sodium sulphide is run in till the zinc is nearly all precipitated. The precipitate is allowed to settle, and a little of the clear liquid removed and added to a drop of an 8 per cent. solution of sodium nitroprusside, further quantities of sulphide being added until the colour appears of equal intensity in the two test mixtures when enough of the supernatant liquid is used to make a pool on the porcelain slab of 30 mm. diameter.

M. J. S.

Estimation of Zinc in Iron Ores. By B. PLATZ (*Zeit. anal. Chem.*, **29**, 342—345; from *Stahl und Eisen*, **9**, 494).—The old method of precipitating the zinc by hydrogen sulphide from an acetic acid solution only gives good results when the amount of zinc is considerable; if the amount is small, iron always precipitates at the same time. The following method achieves the separation completely. Five grams of the ore is dissolved in concentrated hydrochloric acid, and the solution is evaporated with 2 or 3 c.c. of nitric acid and filtered. The strongly acid solution (200 c.c.) is heated to 80—100° and saturated with hydrogen sulphide. If copper is to be estimated, any precipitate obtained may be filtered off. Acetic acid and ammonium acetate are added, and ammonia is run in from a burette, the point of which dips into the liquid, until the precipitate becomes permanently greyish. The grey colour is removed by cautious addition of hydrochloric acid (1 : 50) and then again very dilute ammonia added until the very faintest permanent grey is obtained. At the right point for stopping the addition of ammonia, the precipitate aggregates and begins to subside. It is filtered off and washed with water containing acetic and hydrosulphuric acids. The filtrate should remain clear on further addition of ammonia. The precipitate is dissolved in hydrochloric acid (1 : 6) and the solution filtered. The hydrogen sulphide is expelled by heating, and to the cold solution sodium carbonate is added in slight excess. The mixture is then heated to boiling and filtered. The precipitate obstinately retains alkaline salts, but as, when thrown down in this way, it subsides and filters well, it can be completely washed in an hour. When copper, cobalt, and nickel are absent, the zinc sulphide may at once be ignited with sulphur in hydrogen.

M. J. S.

Estimation of Zinc in presence of Iron and Manganese. By RIBAN (*Compt. rend.*, **110**, 1196—1199).—The liquid is diluted so that it contains not more than 0·1 gram of zinc in 100 c.c. and sodium carbonate is added until a slight precipitate persists, the precipitate being then dissolved by the addition of a few drops of dilute hydrochloric acid. A current of hydrogen sulphide is passed into the cold liquid until the greater part of the zinc is precipitated together with sulphur separated by the action of the ferric salt. A large excess of a solution of sodium dithionate is then added, and the passage of the gas is continued; the zinc is completely precipitated and the iron remains in solution. If the iron is subsequently to be precipitated by ammonia, it is better to use ammonium dithionate, since the ferric hydroxide is very apt to retain alkaline salts. For the same reason, the solution should be neutralised with ammonium carbonate, which should be added until the yellow colour of the liquid begins to change to orange.

After washing with water containing hydrogen sulphide, the precipitate is dried, heated with sulphur in a current of hydrogen, and weighed. It is then dissolved in hydrochloric acid, mixed with a few drops of nitric acid, a large quantity of ammonium chloride added, and then an excess of ammonia. The minute quantity of iron carried down by the zinc is thus precipitated; its weight rarely amounts to 0·002 gram. The examples given are very satisfactory. The method is applicable in presence of calcium salts, since calcium dithionate is soluble.

In order to estimate the iron in the filtrate, it is peroxidised with nitric acid, which has little action on the dithionate, and is precipitated in the usual way. C. H. B.

Detection and Estimation of Antimony and Arsenic. By J. THIELE (*Chem. Centr.*, 1890, i, 877—878; from *Apoth. Zeit.*, **5**, 86—87).—According to the author's experiments, metallic antimony is so far soluble in water that a serious error is caused if washed with hot water previously to weighing it as metal; a partial oxidation also takes place. If the washing is conducted in an atmosphere of hydrogen in presence of electrolytically deposited iron, the solution of the metal is prevented, but this takes from the method its great recommendation, namely, that the antimony is in a directly weighable condition, and necessitates the separation of the iron from the antimony.

As a reagent for the detection of arsenic, hypophosphorous acid will detect 0·05 milligram of arsenious anhydride in 5—10 c.c. of solution. If a small crystal of potassium iodide is added, the reaction becomes still more delicate, 0·025 milligram being detectable. Copper interferes with the reaction. In presence of bismuth and antimony, the precipitate is brought into solution by hydrochloric acid and bromine, omitting the potassium iodide from the reaction. In presence of iron, the solution must be excluded from the air.

In applying Marsh's apparatus to the detection of arsenic in presence of antimony, the author finds that if electrolytically deposited iron is used, no antimony hydride is formed, and this enables small quantities of arsenic to be detected in the presence of

antimony, 0·015 milligram having been detected. If arsenic acid is precipitated in a slow current of hydrogen sulphide in the cold, arsenic trisulphide is formed; if the solution is hot, and the current of hydrogen sulphide is rapid, arsenic pentasulphide is precipitated.

J. W. L.

Loss of Nitrogen in the Analysis of Guanidine and Biguanidine Compounds by Will and Varrentrapp's Method. By J. Freydl (*Monatsh.*, 11. 120—128).—A series of experiments shows that the deficiency of nitrogen found in the analysis of guanidine and biguanidine compounds by the method of Will and Varrentrapp is mainly due to the oxidation of some of the ammonia formed (compare Makris, *Annalen*, **184**, 371). The presence of minute traces of cyanic acid in the soda-lime at the close of the operation also accounts for some slight loss of nitrogen. G. T. M.

Detection of Nitrobenzene. By J. Morpurgo (*Chem. Centr.*, 1890, i, 879; from *Pharm. Post.*, **23**, 258—259).—For the detection of nitrobenzene in bitter almond oil, a specimen is warmed with manganese dioxide and sulphuric acid. Under these circumstances, nitrobenzene does not lose its odour, but after a time it smells of oil of cinnamon; bitter almond oil, on the contrary, develops a disagreeable odour at first, which soon disappears altogether.

In the case of liquors, soaps, &c., calcium hydroxide is added (in the case of a solution, after concentration), warmed, and after allowing to cool, the mass is extracted with ether, the ether distilled off, the residue treated with a little water, two drops of liquid phenol (10 pts. of water : 100 of crystallised phenol) three drops of water, and a piece of potash the size of a pea added, and the mixture warmed carefully. If nitrobenzene is present, a carmine ring forms on the edge of the liquid which becomes green on the addition of bleaching powder. J. W. L.

Examination and Valuation of Spirituous Liquors. By W. Fresenius (*Zeit. anal. Chem.*, **29**, 283—317).—The problem of discriminating a genuine brandy, rum, or other spirituous beverage from an artificial product by chemical methods is beset with peculiar difficulties, both because no consensus of opinion exists as to a definition of a genuine spirit, and because, in the majority of cases, analysis is incompetent to distinguish between articles admitted on all hands to be genuine and those manufactured wholly from foreign ingredients. The author, being in possession of specimens of known character, has analysed them with the following results (p. 1195).

Of the cognacs, Nos. 2 and 3 were fine sorts 15 years old; 1, 4, and 5 were also fine brands, but somewhat younger; 6 and 7 still younger, and originally less alcoholic; 8 had been slightly coloured with caramel.

The rums were all Jamaica rums, but No. 4 had been mixed with one-sixth of pure spirit of wine.

Nos. 1 and 2 of the arracks were from Batavia, the latter mixed with one-sixth of refined spirit; No. 3 was from Sourabaya. Of the Kirschwasser samples, Nos. 1, 2, 3, 4, and 10 were distilled in 1887;

	No.	Specific gravity at 15·5°.	Alcohol per cent. by weight.	Extractive matter.	Mineral matter.	Free acid calculated as acetic acid.	Substances reducing Fehling's solution. Expressed as inverted sugar. In original spirit.	Substances reducing Fehling's solution. Expressed as inverted sugar. After inversion.	Substances reducing Fehling's solution. Difference expressed as cane-sugar.
			By distillation.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
Cognac.	1	0·9332	44·57	1·020	0·014	0·044	0·742	0·919	0·168
	2	0·9314	46·12	0·562	0·016	0·089	0·283	0·380	0·090
	3	0·9327	44·78	0·521	0·021	0·081	—	—	—
	3	0·9380	43·70	1·135	0·012	0·060	0·771	0·971	0·190
	5	0·9393	43·76	1·483	0·005	0·030	0·702	1·351	0·617
	6	0·9324	45·80	0·499	0·001	0·028	0·188	0·451	0·250
	7	0·9378	42·71	0·461	0·004	0·026	—	—	—
	8	0·9365	43·70	0·505	0·004	0·026	—	—	—
Rum.	1	0·8735	69·97	0·680	0·007	0·089	0·368	0·507	0·132
	2	0·8735	69·61	0·611	0·006	0·093	0·324	0·329	0·005
	3	0·8811	66·02	0·339	0·007	0·139	0·144	0·178	0·033
	4	0·8745	68·83	0·495	0·005	0·089	0·257	0·267	0·010
			from sp. gr.						
Arrack.	1	0·9132	52·14	0·062	0·004	0·180	—	—	—
	2	0·9139	51·83	0·067	0·008	0·122	—	—	—
	3	0·9141	51·75	0·161	0·016	0·087	—	—	—
Kirschwasser.	1	0·9343	42·62	0·009	0·002	0·141	—	—	—
	2	0·9293	44·96	0·009	0·002	0·080	—	—	—
	3	0·9177	50·22	0·009	0·002	0·102	—	—	—
	4	0·9199	49·70	0·009	0·002	0·059	—	—	—
	5	0·9336	42·95	0·023	0·005	0·198	—	—	—
	6	0·9258	46·55	0·014	0·002	0·093	—	—	—
	7	0·9236	47·55	0·007	0·001	0·070	—	—	—
	8	0·9325	43·48	0·018	0·005	0·210	—	—	—
	9	0·9242	47·27	0·017	0·011	0·050	—	—	—
	10	0·9347	42·43	0·011	0·003	0·157	—	—	—
	11	0·8975	59·17	0·009	0·003	0·061	—	—	—
	12	0·9697	21·54	0·020	0·006	0·218	—	—	—

8 in 1886; 9 in 1885; 11 in 1883; 5 in 1885 and 1886, and mixed; 3, 4, 6, 7 and 11 were from black cherries; 8 partly from red. No. 12 was 1887 faints (last runnings).

The dark colour of rum was doubtless originally due to the spurting over of some of the still residue, but at the present time it is invariably produced by caramel. Since consumers would not accept it without the dark colour, the addition of caramel cannot be regarded as a falsification. The colouring and extractive matters of cognac are supposed to be wholly derived from the casks in which it is stored, and the quality of the wood for casks is of great importance. The

best is that from Dantzig, Stettin, and Angoulême, as it contains the smallest quantity of bitter principles, and relatively considerable amounts of quercin and quercitrin, to the presence of which aroma and colour respectively are due. Since the absorption of these substances has come to be regarded as a mark of age, young brandy is now almost always slightly coloured by caramel, and a little sugar (generally under 1 per cent.) is added, such additions seeming to be approved by consumers. The presence of such small amounts of added matters in an otherwise genuine brandy cannot be regarded as sufficient to condemn it. But since at some Custom Houses a sweetened spirit is regarded as a liqueur, the practice has grown up of exporting separately the wine distillate and the sugar for sweetening it.

Another, not uncommon, addition is water, and within certain limits this is unavoidable, as the spirit obtained by distillation is often too strong for use. Since, however, spirits stored in wooden casks undergo a loss of alcohol, water is often added to young spirit to give it the appearance of age. More objectionable is the addition of both water and alcohol, but with the lower qualities of rum and arrack it must be regarded as almost the rule. Since these additions impoverish the aroma, it becomes necessary to intensify this by adding various essences, and from this to the manufacture of a wholly factitious product is but a step. The materials added to confer aroma are very various; on the one hand, cognac oil, obtained by the distillation of wine lees, is used, and on the other, ethereal oils and extracts of vanilla, carob pods, tea, almond shells, &c., some of which increase the extractive matters.

The definitions of genuine cognac by various authorities are not in accord; the author considers small additions of caramel and sugar to the wine distillate, with enough water to produce a drinkable spirit, to be admissible, but all beyond this to constitute falsification. With regard to the detection of these additions, that of *caramel*, when in notable quantity, is possible by Amthor's test with paraldehyde and phenylhydrazine (Abstr., 1885, 604); that of *sugar* is more doubtful, since substances reducing Fehling's solution are extracted from the wood of the casks. When, however, the amount exceeds 0·5 per cent., and the reduction is markedly increased by inversion, the presence of sugar may be assumed. The addition of *water* and *alcohol* can only be indirectly inferred from the enfeebling of the aroma, but genuine wine distillates sometimes possess a very feeble aroma. The comparative or total absence of furfuraldehyde is one of the best indications of the absence of the genuine distillate, since this always contains furfuraldehyde, whilst well distilled spirit does not. Little can be done in the detection of artificial aromas, both because few chemical methods are available, and because the nature of the aromatic substances present in genuine spirits is too little known. The author's opinion is that chemical analysis is not competent to decide as to the genuineness of cognac, rum, or arrack, but that the smell and taste, as judged by experts, are by far the best tests. The test relied on by the Custom House authorities, namely, the estimation of the extractive matters, the amount of which is assumed not to exceed 0·5 per cent. in genuine spirits, is highly fallacious, since in the majority of cases

it fails to detect falsifications, whilst at the same time it would condemn the oldest and finest genuine products as adulterated.

The author has repeated his experiments made in 1887 on the increase in volume of chloroform when shaken with cognac, but finds his then conclusions not to be confirmed. The behaviour of different specimens of (so-called) pure spirit of wine is by no means uniform.

M. J. S.

Estimation of Starch in Fodder, &c. By A. LECLERC (*J. Pharm.* [5], **21**, 641—645).—Weigh off 2 grams of powdered grain, or 5 grams of straw, hay, fæces, &c., place in a 200 c.c. flask, and add 10 c.c. of water. It is essential that the assay should be thoroughly moistened in every part. To the moistened mass add 180 c.c. of a neutral zinc chloride solution of sp. gr. 1·450, agitate, and heat in a salt-water bath at 108° for 1 to $1\frac{1}{2}$ hours. In the case of grain, the heating can be stopped when the *débris* has been rendered soluble; for straw, the full $1\frac{1}{2}$ hours should be taken. Cool and transfer to a 250 c.c. flask, making up the volume by the addition of zinc chloride solution; in the case of fibrous fodder, the volume is made up to 253 c.c., to compensate for the volume of the residue. Filter, and of the opalescent filtrate take, say, 25 c.c. in a 150 c.c. beaker, add 2 c.c. of hydrochloric acid to retain the zinc in solution, and then 75 c.c. of 90 per cent. alcohol, or 62 c.c. of 95 per cent. alcohol. Filter through a tared filter after 24 hours. The whole of the dextrin and starch are precipitated; the sugars remain in solution. The precipitate is washed, until free from zinc chloride, with a mixture of 1000 c.c. 90 per cent. alcohol and 5 c.c. of hydrochloric acid; the acid is then washed out with alcohol alone. A little mineral matter taken down by the starch is obtained as ash on burning the starch, and is deducted. A little nitrogenous matter is also present in the case of grain, which can be determined by estimation of the nitrogen. Thus in the quantities given, maize would yield about 1·5 to 2 milligrams of nitrogenous matter in the precipitate from 25 c.c. of solution, oats a little less, and straw not more than 0·5 milligram. The formation of a little dextrin is no inconvenience, as it has the same composition as the starch. The zinc chloride solution is prepared by treating hydrochloric acid with excess of zinc. The decanted solution is decolorised by the addition of a little concentrated potassium permanganate solution, boiled, and treated with zinc oxide as long as any dissolves; after cooling and filtering, the solution is ready for use. J. T.

Test for Aldehyde. By L. CRISMER (*Zeit. anal. Chem.*, **29**, 350—351).—Nessler's reagent is a delicate test for aldehyde and substances of aldehyde function, giving with them a yellowish precipitate, which gradually darkens through reddish-brown to black. It can be distinguished from the precipitate caused by ammonia by the addition of potassium cyanide, which dissolves the ammonia precipitate, but turns the aldehyde precipitate black. Ordinary ether and chloroform are always found to contain aldehyde, but can be completely purified therefrom by treatment with Nessler's reagent and distillation. Hydroxylamine salts also give black precipitates with Nessler's reagent. M. J. S.

Adulteration of Linseed Oil. By A. AIGNAN (*Compt. rend.*, 110, 1273—1275).—Pure linseed oil has no rotatory power, but if mixed with resin oil it turns the plane of polarisation through an angle proportional to the quantity of the latter. If $[\alpha]_D$ represents the rotation observed with a column of oil 20 cm. long, and h the weight of resin oil in 100 parts of the mixture, then with *refined resin oil*, $[\alpha]_D = + 14/15h$; with *selected white resin oil*, $[\alpha]_D = + 17/15h$, and with *finest rectified resin oil*, $[\alpha]_D = + 21/15h$. The first variety is most commonly met with as an adulterant.

In order to detect resin oil in paint, the latter is extracted with ether, and the rotatory power of the ethereal solution measured in a column 20 cm. long. The proportion of resin oil is given by the formula $h = \frac{[\alpha]_D}{43'}$. A known weight, P_1, of the ethereal solution is heated at 100°, in order to expel the ether, and the residual oil, P_2, is weighed; then $P_1/P_2 \times 100 = h$, the total percentage of oil in the ethereal solution. If $h_1 = h$, only resin oil is present; in any other case, $h/h_1 \times 100$ gives the proportion of resin oil in 100 parts of the mixture (compare this vol., p. 422). C. H. B.

Estimation of Codeïne and Morphine. By E. CLAASEN (*Chem. Centr.*, 1890, i, 741; from *Pharm. Rundschau*, 1890, 40).—The author utilises the precipitation of morphine by codeïne from solutions of its salts for the quantitative estimation of the former. (1.) The liquid containing free codeïne is warmed with an excess of morphine sulphate, the liquid is frequently shaken, and the precipitated morphine collected at the end of 24 hours. Its weight, multiplied by 0·9868, gives the amount of anhydrous codeïne; multiplied by 1·0462 gives the amount of codeïne + 1 mol. H_2O. If the codeïne is present, either in the free state, or as a salt with or without the presence of morphine or its salts, the solution is evaporated to dryness with excess of magnesium oxide, the residue is stirred with hot water, and shaken in a flask with ether (free from alcohol); the ether is distilled from the extract, the residue extracted with hot water, filtered, and the codeïne determined in the solution as above described. It is well to wet with benzene the sides of the glass vessel in which the precipitation is conducted. (2.) If *only* free codeïne is present in the solution, its quantity may be determined by boiling it with an excess of ammonium chloride, and collecting the free ammonia, which may be titrated. The amount of ammonia multiplied by 17·588 gives the amount of anhydrous codeïne. (3.) In all other cases where a variety of substances may be present with the codeïne and morphine, the solution is acidified with dilute sulphuric acid, evaporated to dryness with excess of magnesium oxide, the residue is extracted with strong alcohol, the latter distilled off, and the residue heated (as in "2") with excess of ammonium chloride. The liquid remaining in the flask is acidified and the morphine precipitated with a slight excess of ammonia. After filtering off the precipitated morphine, the ammonia is entirely evaporated from the filtrate, when a further small quantity of morphine

separates. Finally the codeïne, which is in the filtrate as hydrochloride, may be determined according to (1). J. W. L.

Analysis of Urine. By K. Taniguti (*Zeit. physiol. Chem.*, **14**, 471—490).—Salkowski has proposed a method of estimating creatinine in urine which was compared in a series of experiments with the older method of Neubauer. The results are sometimes higher by the one, sometimes by the other method.

Creatinine can be detected in the urine after the ammoniacal fermentation has progressed for 61 days.

A substance is present in normal urine which yields acetone when the urine is distilled with sulphuric acid. At least 10 c.c. of concentrated sulphuric acid should be added to 300 c.c. of urine; if less than this amount of acid is used, all the acetone does not come off on distillation. The total distillate is made alkaline with sodium hydroxide; a solution of iodine in potassium iodide is added; and after 24 hours the precipitated iodoform is collected on a weighed filter, dried, and weighed. From the amount of iodoform so obtained, the quantity of acetone obtainable is calculated; various specimens of urine yielded from 0·01 to 0·02 gram of iodoform.

Further experiments confirmed Salkowski's statement (Abstr., 1889, 431) that volatile fatty acids are formed during the ammoniacal fermentation of urine. Quantitative results show that the fatty acids (chiefly acetic) increase with the intensity of the fermentation and the length of time for which it is allowed to occur.

The source of the acid is considered to be the carbohydrate of normal urine. Humous substances are considered by Udránszky (Abstr., 1888, 180) to have a similar origin, but the amount of humous substances does not increase with putrefaction, that is, as the carbohydrate disappears; moreover, the humous substances of stale urine have a different elementary composition from those of normal urine. Salkowski considers Udránszky to be wrong in this and other points. W. D. H.

Estimation of Albumin in Urine. By T. C. Van Nüys and R. E. Lyons (*Amer. Chem. J.*, **12**, 336—351).—The authors first estimate the total quantity of the nitrogen in the urine by Kjeldahl's method. The albumin is then precipitated by means of Almén's solution of tannin, the solution filtered, and the nitrogen determined in a measured quantity of the filtrate. The tannin should not be used in large excess. For ordinary quantities of albumin in urine, equal volumes of Almén's solution and of urine are sufficient; for small quantities, one volume of Almén's solution and two volumes of urine. If 2 per cent. or more of the albumin is present, the urine should be diluted with from one to two volumes of water before making the determination. To separate the albumin, 10 c.c. of the filtered urine is introduced with 10 c.c. of Almén's solution into a 50 c.c. flask, and, after mixing well, the liquid is filtered through a dry filter-paper into a dry beaker. 5 c.c. of this solution is subjected to the action of 10 c.c. of concentrated sulphuric acid, as in Kjeldahl's original method. To absorb the ammonia, 10 c.c. of

$\frac{1}{5}$ normal potassium hydroxide solution is employed. If the number of c.c. of $\frac{1}{5}$ normal potassium hydroxide solution employed in the two determinations be subtracted, and the difference multiplied by $0{\cdot}0028 \times 40 \times 6{\cdot}37$, the product is the percentage of albumin contained in the urine.

The results of a number of analyses are given, and these show that the method is an exact one. It has, moreover, the advantage of giving the total nitrogen contained in the urine, which may be a matter of importance to the pathologist. G. T. M.

Detection of Carbonic Oxide Hæmoglobin. By A. WETZEL (*Chem. Centr.*, 1890, i, 738—739; from *Ver. phys. med. Gess. Wurzburg*, **23**).—The author recommends the following tests for carbonic oxide hæmoglobin:—10 c.c. of the blood, 15 c.c. of ·20 per cent. potassium ferrocyanide solution, and 2 c.c. of acetic acid (1 vol. glacial acetic acid : 2 vols. water) are mixed, and shaken gently. Coagulation ensues, the mass gradually becoming solid. If normal blood only is present, it is dark-brown coloured; if it is carbonic oxide blood, the colour is light-red. In the latter case, the colour of the mass becomes gradually dark-brown at the top, this change proceeding gradually to the bottom. If only very little blood is at hand, it is diluted with 4 to 10 vols. of water, and to 10 c.c. of this, 5 c.c. of the potassium ferrocyanide, and 20 drops of the acetic acid are added.

A second test is:—the blood is diluted to 4 vols. with water, to which 3 vols. of 1 per cent. tannin solution is added, and the mixture shaken. At the end of 24 hours, normal blood has a grey colour, whilst carbonic oxide blood becomes carmine-red. This test is very delicate, and 0·0023 per cent. of carbonic oxide in the air was detected by its means.

The author finds that a blood containing 26·5 per cent. of carbonic oxide blood causes a single wide band in the spectrum. In order to apply this to the quantitative determination of carbonic oxide in blood, he dilutes a blood containing more than the above amount of carbonic oxide with normal blood until the band appears singly.

J. W. L.

Reactions of Carbonic Oxide Blood. By E. RICHTER (*Chem. Centr.*, 1890, i, 730; from *Deutsche med. Wochschr.*, **16**, 199).—The following three reactions are recommended by the author, all of which depend on the stability of carbonic oxide blood:—(1) 3 c.c. of this blood and of normal blood are diluted with 100 c.c. of water, and to 10 c.c. of the solution 2 c.c. of 2 per cent. grape-sugar solution is added, then 2 c.c. of lime-water, and the mixture warmed. (2) To the same diluted blood and 2 c.c. of sugar solution, barium carbonate is added, and the mixture warmed. (3) 5 c.c. of each blood is diluted to 200 c.c., 2 drops of yellow ammonium sulphide, and then 6 drops of 50 per cent. formic acid added. In all these tests, the carbonic oxide blood is not changed, whilst normal blood is discoloured. Tartaric, lactic, or phosphoric acid may be substituted for the formic acid in the last reaction. J. W. L.

General and Physical Chemistry.

Molecular Refraction of Nitrates. By R. LOEWENHERZ (*Ber.*, **23**, 2180—2182).—The author has measured the refractive power of ethyl, propyl, isobutyl, and amyl nitrates; his results show that nitrogen is quinquavalent in all these compounds. F. S. K.

Relation between the Molecular Refractive Energy and the Dispersive Power of Aromatic Derivatives with Saturated Lateral Chains. By T. COSTA (*Gazzetta*, **19**, 478—499).—Nasini (*Rend. Acad. Lincei*, 1887, **3**, 168; and Abstr., 1887, 626) showed that in compounds containing an aromatic nucleus with saturated lateral chains, the molecular refractive energy increases and the dispersion diminishes with the number of carbon-atoms in the lateral chain; these compounds thus present the most considerable differences between the observed refractive energies and the results of calculation by Brühl's law. The author has prepared the following compounds of this class, which combine as far as possible a low dispersive power and a high refractive energy, with the view of discrediting Brühl's generalisations:—

Diisoamylbenzene, $C_6H_4(C_5H_{11})_2$, prepared by Austin's method (*Bull. Soc. Chim.*, **31**, 12), is a colourless, limpid oil, boiling between 253·7° and 264·2° (corr.), under a pressure of 747 mm. (corr.); vap. den. 7·64. *Amylthymol*, $C_6H_3PrMe{\cdot}OC_5H_{11}$, prepared by heating amyl iodide with potassium thymol under pressure, is a colourless liquid, boiling between 242° and 243° (corr.) at 746·51 mm. (corr.); vap. den. 7·57; mol. wt. 220 (see Engelhardt and Latschinoff *Bull. Soc. Chim.*, **13**, 148). *Amyleugenol*, $C_3H_5{\cdot}C_6H_3(OMe){\cdot}OC_5H_{11}$, is a colourless liquid, boiling with incipient decomposition between 300·6° and 301·7° (corr.) at 746·51 mm. (corr.); vap. den. 8·17; mol. wt. 234 (see Cahours, *Compt. rend.*, 1877, 151, 1195). *Diamylresorcinol*, $C_6H_4(OC_5H_{11})_2$, is a crystalline solid, soluble in water, and melting at 47°; mol. wt. 250. *Amyl-α-naphthol*, $C_{10}H_7{\cdot}OC_5H_{11}$, is a colourless liquid, which turns yellow and red on exposure to light. It boils with decomposition between 317 and 319° (corr.) at 741·9 mm. (corr.); mol. wt. 214. *Amyl-β-naphthol*, $C_{10}H_7{\cdot}OC_5H_{11}$, is a faintly yellow liquid, rapidly altered by exposure to light. It boils with decomposition at 323—326° (corr.) at 759·3 mm. (corr.). The last four compounds are prepared in a manner analogous to amylthymol. The following table exhibits the results obtained, and it is noteworthy that in many cases where the dispersion is less than that of cinnamic alcohol, the differences between the calculated and observed values of the molecular refractive energy are greater than the value assigned by Brühl to the presence of an atom of some of the elements or of a double or triple linkage:—

	Diamyl-benzene.	Amyl-thymol.	Amyl-eugenol.	Diamyl-resorcinol.	Amyl-α-naphthol.	Amyl-β-naphthol.
Temperature	15·2°	14·15°	14·8°	10·1° Benz. Sol.	14·2°	12·00°
$d\frac{t}{4}$	0·87446	0·90346	0·97291	0·89459	1·00689	1·01555
μ_{Li}	1·49230	1·48778	1·50786	1·50047	1·56288	1·56915
μ_α	1·49317	1·48831	1·50856	1·50136	1·56404	1·57032
μ_{Na}	1·49673	1·49230	1·51284	1·50601	1·57049	1·57679
μ_{Tl}	1·50069	1·49633	1·51775	1·51118	1·57806	1·58452
μ	1·50587	1·50174	1·52386	1·51801	1·58808	1·59485
μ_γ	1·51397	1·51019	1·52990	1·52832	—	—
$\frac{\mu_\alpha - 1}{d}$	0·56397	0·54048	0·52272	0·52220	0·56020	0·56158
$P\frac{\mu_\alpha - 1}{d}$	122·9	118·90	122·32	130·55	119·88	120·18
R_α	121	116·2	118·8	126·6	113·2	113·2
Differences	1·9	2·7	3·52	3·95	6·68	6·98
$\frac{\mu_\alpha^2 - 1}{(\mu_\alpha^2 + 2)d}$	0·33243	0·31907	0·30667	0·30755	0·32307	0·32321
$P\frac{\mu_\alpha^2 - 1}{(\mu_\alpha^2 + 2)d}$	72·46	70·19	71·76	76·88	69·13	69·17
R'_α	72·06	69·08	70·36	75·22	66·40	66·40
Differences	0·4	1·11	1·40	1·67	2·73	2·76
$\frac{\mu_\gamma - \mu_{Li}}{d}$	0·02478	0·02484	0·02265	—	—	—
$\frac{\mu_\beta - \mu_{Li}}{d}$	—	—	—	—	0·02503	0·02531
$\frac{\mu_\gamma - \mu_\alpha}{d}$	0·02378	0·02422	0·02193	0·02309	—	—
$\frac{\mu_\beta - \mu_\alpha}{d}$	0·01452	0·01486	0·01572	0·01383	0·02387	0·02415
$\frac{\mu_\gamma^2 - \mu_{Li}}{\mu_\gamma^2 - 1}$	0·05042	0·05245	0·04998	—	—	—
$\frac{\mu_\gamma^2 - 1}{\mu_\alpha^2 - 1}$	1·05087	1·05399	1·05083	—	—	—
$\frac{\mu_\beta^2 - \mu_\alpha^2}{\mu_\beta^2 - 1}$	0·03005	0·03198	0·03508	—	0·04980	0·05031
$\frac{\mu_\beta^2 - 1}{\mu_\alpha^2 - 1}$	1·03098	1·03303	1·03635	—	1·04241	1·05297

S. B. A. A.

Violet Flame produced by Common Salt in a Coal Fire. By A. P. Smith (*Chem. News*, **61**, 292—293; compare Abstr., 1879, 497; 1889, 336).—The author maintains that the violet flame produced by common salt in a coal fire is due to the chlorine, both for grounds already stated, as well as on the evidence of the spectrum of the flame, and that it is not due to copper, as suggested by Salet (this vol., p. 560).

D. A. L.

Phosphorescence produced by the Contact of Ozone with certain Waters. By E. Fahrig (*Chem. News*, **62**, 39—40).—The author has observed a transitory soft phosphorescent glow, in the dark, when some samples of water are brought into contact with

ozone, or with ozonised water, oil, or air; neither chlorine nor hydrogen peroxide produces the phenomenon, nor do all waters; for instance, a deep well water and sea water did not, whilst river water did; moreover, boiling and filtering the water did not destroy the power of producing the phosphorescence. Some suggest oxidation of organic matter and organisms as the cause. D. A. L.

Electrical Conductivity of Solutions of Cadmium Salts. By F. J. WERSHOVEN (*Zeit. physikal. Chem.*, 5, 481—525).—Solutions of cadmium chloride, bromide, iodide, nitrate, and sulphate, and potassium cadmium oxide were investigated by the author within wide limits of concentration and temperature. The temperature-coefficient of all the salts, except the iodide and double iodide, approximates at extreme dilutions to 2·3 per cent. per degree. In concentrated solutions, the variations of conductivity with the temperature may be expressed by a linear equation in the case of the chloride, iodide, and double iodide; the other salts require an equation of the second degree. Differences of as much as 10 per cent. sometimes appear between Grotriau's numbers and the conductivities found by the author; these the latter attributes to the "not quite perfect purity" of his preparations. A long discussion of the results with respect to molecular conductivity, the rate of transference of the ions, and the supposed complexity of the salt-molecules is entered on. The author concludes with Arrhenius that in cadmium nitrate the inactive molecules are not complex, but that in the other salts they are. Combined with Kohlrausch's values for the speed of migration of the anions Cl, Br, I, and NO_3, the numbers obtained for extreme dilutions give the following speeds of the cadmium ion:—49·2, 50·9, 49·3, 53·7; in the mean, 51. The speeds of other ions (bivalent metals) in the same units are: barium, 51; zinc, 51; magnesium, 53.

In the course of his experiments, the author found that a freshly-platinised platinum electrode, when dipped into a solution of potassium iodide, coloured the solution at first yellow, and, after a few minutes, pink. The coloration is due to platinum tetriodide dissolved in the solution of potassium iodide, and not in any way to iodine, as was proved by the addition of starch solution. The action seems to be $PtCl_4 + 4KI = PtI_4 + 4KCl$. It is not necessary that the electrode should have been previously immersed in a solution of platinum chloride; hydrochloric acid alone effects the reaction, which indeed may be used as a most delicate test for this acid, yielding results when silver nitrate gives no turbidity. For this purpose, the washed platinised electrode is dipped repeatedly into potassium iodide solution until it no longer gives the pink colour; it is then washed thoroughly with alcohol and water, allowed to remain for some time in the solution to be tested for hydrochloric acid, is again washed, and reimmersed in dilute potassium iodide solution. After some time, the pink colour appears. Chlorides, or hydrobromic and other acids, do not give the coloration. J. W.

Electrolysis of Various Substances. By P. L. ASLANOGLOU (*Chem. News*, 62, 42—43).—The current from six Fuller's mercury

dichromate elements was passed through various solutions with the following results:—Water containing calcium, magnesium, barium, strontium, or zinc hydrogen carbonate yielded a deposit of the normal carbonate at the negative electrode, both oxygen and hydrogen being evolved in all cases. Ferrous carbonate remained unaltered under similar treatment, although the evolution of the gases was the same. Silver chloride dissolved in sodium thiosulphate gave a deposit of metallic silver and an odour of hydrogen sulphide with an evolution of hydrogen but no oxygen. Lead sulphate dissolved in ammonium tartrate deposited a black mass, smelling of ammonia, at the negative pole, while the positive pole and the liquid became yellow and both oxygen and hydrogen were evolved. D. A. L.

Amalgams. By M. LE BLANC (*Zeit. physikal. Chem.*, **5**, 467—480). —This paper contains an investigation of the magnitude of the polarisation given by various amalgams in a solution of the corresponding chloride against zinc amalgam. The apparatus used included a large tuning-fork, which by its vibrations allowed measurements of the E.M.F. of polarisation to be made while the primary current was practically constantly flowing. The rate of fall of the polarisation after the primary current was interrupted gave a means of estimating the relative stability of the amalgams. Amongst those of the metals of the alkalis and alkaline earths, lithium and magnesium amalgams are the least stable. After the current from eight Leclanché cells had passed for ten minutes, the evolution of gas was in general feeble, but in the case of lithium and magnesium, it was comparatively lively. The author found that in a mixture of zinc chloride and hydrogen chloride solutions, zinc amalgam was formed at the negative pole, which would indicate that *atomic* hydrogen displaces zinc in its salts. The ammonium and alkylammonium amalgams are proved to have an actual existence, for the phenomena observed with solutions of the ammonium chlorides are quite comparable with those obtained when metallic chlorides are employed. These amalgams, however, are much less stable, as is seen by the relatively rapid falling-off of the E.M.F. of polarisation when the primary current ceases to flow. Besides ammonium, the author investigated methyl-, ethyl-, dimethyl-, diethyl-, trimethyl-, triethyl-, and tetramethyl-ammonium amalgams. Triethylammonium amalgam probably does not exist—it is at any rate extremely unstable; trimethyl- and diethyl-ammonium form amalgams scarcely less so. The formation of a mercury froth on electrolysis has hitherto been held as a good indication of the production of an amalgam, but it is pointed out by the author that in the case of ethylammonium there is no froth, and yet the electrical behaviour shows that a comparatively stable amalgam is formed. J. W.

Melting Points of Organic Compounds. By A. REISSERT (*Ber.*, **23**, 2239—2245).—The author has tried to ascertain under what conditions the melting point of a substance can be determined with constant results; his experiments in this direction were not successful, but it was found that, if in taking the melting point in a

capillary tube the following three rules are observed, the errors of observation are considerably diminished.

(1.) The zero point of the thermometer should be determined from time to time, and the proper correction made if necessary.

(2.) The correction for the projecting thread must always be made, otherwise there may be a difference of several degrees between the melting points found by different observers; Rimbach's tables (this vol., p. 205) are convenient for this purpose.

(3.) The temperature at which the substance commences to melt should be noted and not that at which it is completely liquefied.

The corrected melting points of 24 pure substances, ranging from paraxyleue (m. p. 13°) to anthraquinone (m. p. 284·65°) are given.

F. S. K.

Deductions from Van't Hoff's Theory. By S. Pagliani (*Gazzetta*, 19, 453—478; compare this vol., p. 845).—The author has calculated the value of i from Van't Hoff's equation

$$i = \frac{Q}{2t^2} \div \frac{2d \log C}{dt} \ldots\ldots\ldots (1),$$

for solutions at various temperatures and of different degrees of concentration of the salts K_2SO_4, $NaNO_3$, KCl, NH_4Cl, KNO_3, and $NaCl$. The figures obtained lead to the conclusion that the above equation is wanting in generality, the values of i diminishing with the increase of concentration contrary to the theory. If (1) were in general true, Q and $\frac{d \log c}{dt}$ would have the same sign; in other words, the solubility of a salt and its heat of dissolution at different temperatures would always vary in the same sense, a generalisation to which there are very numerous exceptions.

These discrepancies are probably due to the dependence of Van't Hoff's equation on the general laws of equilibrium in solutions, the second of which assumes that the transformation of one system into another takes place at constant volume, an assumption which does not hold in solutions of salts.

A comparison of (1) with the equation deduced from the diminution of the vapour tension of the solution of a salt, shows that if salts are considered to be in solution in the anhydrous state, Van't Hoff's equation is either in conflict with experimental results, or with Kirchhoff's theoretical deductions (*Ann. Phys. Chem.*, 1858, 194, and 1885, 24; Abstr., 862, 1885); the discrepancies may, however, be explained by assuming that the salts possess a different degree of hydration at different temperatures. Similarly, on comparing (1) with the equation $i = \frac{1}{18 \cdot 5} \frac{M\Delta}{p}$ (where M is the molecular weight, and Δ the depression of the freezing point produced by a quantity p in solution), it appears that, whereas i always diminishes with increase of concentration when calculated from the former equation, the value of $\frac{\Delta}{p}$ increases or diminishes with the concentration according to the nature of the salt; to reconcile the equa-

tions, it is necessary to suppose that M uniformly decreases with increasing concentration to an extent sufficient to render the variation of $\frac{\Delta}{p}$ insignificant.

The absorption of heat which in many cases takes place during dissolution, and which increases with the increase of dilution of the solution and with the diminution of the temperature of the solvent, just as the state of hydration of a salt is supposed to do, is explained by the author by the assumption that the quasi-aëriform condition in which, by Van't Hoff's theory, salts are supposed to exist in dilute solutions, necessitates the absorption of a certain quantity of heat of dilatation. S. B. A. A.

Thermal Behaviour of Cupric Chloride Solutions. By L. T. Reicher and C. M. van Deventer (*Zeit. physikal. Chem.*, **5**, 559—565). Le Châtelier and Van't Hoff deduced as a necessary consequence of thermodynamics that when the heat of dissolution of a substance in its almost saturated solution was negative, the solubility would increase with increase of temperature; when positive, the solubility would diminish with rise of temperature. The salt $CuCl_2,2H_2O$ is one of the few which dissolve in much water with development of heat, and its temperature coefficient of solubility is positive. These facts, when taken in conjunction with the above principle, would point to curious behaviour of the salt with respect to the heat of dissolution in liquids of different concentration. The authors have investigated the matter experimentally, and find that in a saturated solution, the heat of dissolution is negative, as theory predicts. From observations of their own, and from data given by Thomsen as to the heat of dilution of cupric chloride solutions, they calculate that the heat of dissolution attains a maximum (at 11°) when the solvent has a strength of about 8 mols. of $CuCl_2,2H_2O$ to 198 mols. of H_2O. At this concentration, therefore, the salt would be dissolved without any thermal effect whatever, and direct experiment confirms this conclusion. The heat of dissolution becomes negative when the concentration is about 18 mols. of salt to 198 mols. of water. J. W.

Heat of Combustion and Constitution of Organic Compounds. By O. Dieffenbach (*Zeit. physikal. Chem.*, **5**, 566—588). —The author subjects the heats of combustion of various organic compounds to an arithmetical investigation, and from his results seeks to draw conclusions as to the constitution of the substances in question. As the basis of calculation he assumes that the heat of combustion of a compound is additively made up of certain values which are constant for all compounds. Thus we have the heat of combustion of the "isolated" carbon-atom, of the hydrogen-atom attached to carbon, and of the various forms of linking between the carbon-atoms. All these constants may, from the experimental data, be expressed in terms of any one: the fatty single bond is chosen as the standard by the author. Reckoning in this way, he finds that what is left over for carbon linking in the benzene nucleus is equal to the thermal value of nine single bonds, and bears no simple relation to

three single and three double bonds: he thus considers it highly probable that the six carbon-atoms in the benzene ring are connected by nine single bonds, and that Kekulé's formula is erroneous. Similarly, the heat of combustion of naphthalene would point to its ten carbon-atoms being connected by sixteen single bonds. The six carbon bonds in hexamethylene (hexahydrobenzene) appear to be ordinary fatty bonds; but the three in trimethylene are not so.

By making sundry more or less probable assumptions, the author endeavours to fix limits between which the value of his standard must lie, and comes to the conclusion that the value for the single bond must be greater than 15000 cal. and less than 48000 cal. Further, the relations between the various kinds of linking are found to be—

$$\begin{aligned} \text{double} &= 2 \text{ single} - 15193 \text{ cal.} \\ \text{triple} &= 3 \text{ single} - 3 \times 14952 \text{ cal.} \\ 2 \text{ trimethylene} &= 2 \text{ single} - 15286 \text{ cal.} \end{aligned}$$

The numerical terms in these equations are approximately multiples of 15000, so that the author thus thinks it probable that the absolute valnes of the constants are also multiples of such a number. That being the case, the only values which satisfy the limits he found above are—

$$\begin{aligned} \text{single} &= 30300 \text{ cal.} \\ \text{double} &= 45450 \text{ cal.} = \tfrac{3}{2} \text{ single} \\ \text{triple} &= 45450 \text{ cal.} = \tfrac{3}{2} \text{ single} \\ \text{trimethylene} &= 22725 \text{ cal.} = \tfrac{3}{4} \text{ single.} \end{aligned}$$

The thermal value of the double bond would thus be equal to that of the triple bond. Further, the heat of combustion of the "isolated" carbon-atom would be 166573 cal., and of the hydrogen-atom attached to carbon, 11039 cals. By the help of these values, the author calculates the heat of combustion of several compounds not used in obtaining the numbers, and finds a satisfactory agreement with direct experiment. J. W.

The "Dead Space" in Chemical Reactions. By O. LIEBREICH (*Zeit. physikal. Chem.*, **5**, 529—558).—In a communication to the Royal Prussian Academy, the author pointed out that certain parts of the liquid in which a slow chemical transformation is going on exhibit either no reaction, or a diminished or delayed reaction. This peculiar region he terms the dead space, and in the present paper seeks to ascertain the cause of the phenomenon. For the purposes of experiment, the most useful reactions are the transformation in dilute aqueous solution of chloral into chloroform by means of sodium carbonate, and the reaction between iodic acid and sulphurous acid. In the first case, the extent of the reaction is rendered visible by the separation of chloroform; in the second case, by the liberation of iodine.

The dead space appears at the free surface of the liquid, and is easily visible to the naked eye; and in narrow spaces, capillary tubes for example, there is either retardation or entire prevention of tho reaction, as may be seen when iodic and sulphurous acids are used

along with starch solution. In somewhat wider tubes, a thin thread of blue appears in the last case along the axis. Some 40 figures are given in the paper to show the form of the dead space in vessels of various shapes.

The author proves conclusively that the dead space at the free surface is not due to evaporation, and is inclined to attribute the phenomenon to the physical influence of the walls and to the surface tension, there being a certain viscosity to hinder the reaction in these regions. This view receives support from the fact that the dead space diminishes in extent with rise of temperature. J. W.

Influence of Glass Surfaces on Velocity of Reaction. By SPERANSKI (*Zeit. physikal. Chem.*, 5, 607—608).—The observation of Liebreich (preceding abstract), that the reaction between iodic and sulphurous acids did not take place when the mixture was poured into a vessel filled with glass beads, points to a possible source of error in the determination of many velocities of reaction. The author studied the influence of glass wool and glass beads on the rate of inversion of cane-sugar by hydrochloric acid. Glass wool produced a continuous diminution of the velocity-constant, but this was proved to proceed from interaction between the glass and the acid, the titre falling to about half its initial value in three days. Beads previously boiled in acid exerted not the slightest influence on the rate of inversion. J. W.

Isomorphism. Part II. By J. W. RETGERS (*Zeit. physikal. Chem.*, 5, 436—466).—In a former paper (this vol., p. 328), the author studied the nitrates of the alkali metals and of silver. He now takes up and investigates in detail the corresponding chlorates, the method employed being, as before, a study of the specific gravities of the mixed crystals.

In the isodimorphous series [$AgClO_3 : NaClO_3$], crystals containing up to 18·2 per cent. of silver chlorate are regular; a break in the series then follows, after which crystals containing more than 71·5 per cent. of the silver salt are quadratic. Potassium and silver chlorates crystallise very sparingly with each other, the monoclinic potassium salt taking up only a small fraction of a per cent. of silver salt, which in its turn behaves similarly towards the former. A quadratic double salt, $KClO_3,AgClO_3$, is, however, formed when the simple salts are allowed to crystallise in molecular proportions. Sodium and potassium chlorates neither form a double salt, nor do they take up more than traces of each other when they crystallise from mixed solutions. The chlorates of ammonium, rubidium, cæsium, and thallium are all considered by the author to be monoclinic and isomorphous with potassium chlorate. Lithium chlorate is probably rhombic. A table is given comparing the nitrates, chlorates, bromates, and iodates of the above metals.

The author, in conclusion, criticises the value of identity of angle, parallel growth, &c., as criteria of isomorphism; and is of opinion that only a study of the capability in any given case to form mixed crystals can lead to definite and trustworthy results. J. W.

Freezing Point of Isomorphous Mixtures. By F. W. KÜSTER (*Zeit. physikal. Chem.*, 5, 601—606).—It is well known that Van't Hoff's law for the depression of the freezing point holds true only when the solvent separates out as such. If some of the dissolved substance crystallises along with the solvent on freezing, then the law is no longer applicable (Van't Hoff, this vol., p. 1044), but must be suitably altered. The author investigates a combination of substances which crystallise together in all proportions, namely, hexachlor-α-keto-γ-pentylene, C_5Cl_6O, and pentachlormonobrom-α-keto-γ-pentylene, C_5Cl_5BrO. Here the crystals which separate have the same composition as the liquid, and the freezing point may be calculated from the simple formula of mixing, that is, the curve of the freezing point tabulated against percentage composition of the mixture is a straight line joining the freezing points of the two pure substances. J. W.

Affinity-constants of Organic Acids. By H. G. BETHMANN (*Zeit. physikal. Chem.*, 5, 385—422).—In this paper we have a further contribution to the determination of the constants of affinity which have been shown by Ostwald (Abstr., 1889, 818) to be so characteristic for the various organic acids. The author has measured the constants of over 40 additional substances, including substituted benzoic acids, the polycarboxylic acids of benzene, naphthoic and hydronaphthoic acids, many bibasic acids of the oxalic series, and one or two derivatives of pyridine and thiazole.

The alkyl substitution-products of succinic and glutaric acids are the subject of a special discussion from the point of view of the Van't Hoff-Wislicenus theory. The substitution of a hydrogen-atom by a methyl-group usually lowers the constant, but in succinic acid, &c., the opposite is the case. From a consideration of the numbers obtained by him for the different derivatives, the author is disposed to believe that the raising of the constant in such instances is due to approximation of the two carboxyl-groups, brought about by the introduction of the compound radicle. J. W.

Inorganic Chemistry.

Ammonia in Burnt Magnesium. By P. L. ASLANOGLOU (*Chem. News*, 62, 99).—Ammonia was observed in the magnesium hydroxide left behind after burning magnesium wire or dust in the air.

D. A. L.

Water of Crystallisation. By L. SCHNEIDER (*Monatsh.*, 11, 166—178).—In his investigations, the author considers, as water of crystallisation, only that water which is directly taken up by the anhydrous salt, and which can be driven off on heating the compound. Supposing the density of the anhydrous salt to remain constant when in combination, it appears that water, existing as water of crystallisation, has a constant density of either $\frac{6}{5}$ or $\frac{4}{3}$. The

former number obtains in the case of the following compounds:—$NaBr,2H_2O$; $BaCl_2,2H_2O$; $SrCl_2,6H_2O$; $Na_2CO_3,10H_2O$; $2NaOH,7H_2O$; $CaSO_4,2H_2O$; $Al_2(SO_4)_3,18H_2O$; $Na_2B_4O_7,5H_2O$; $Ca(NO_3)_2,4H_2O$; $K_2Al_2(SO_4)_4,24H_2O$; $(NH_4)_2Al_2(SO_4)_4,24H_2O$; $Na_2Al_2(SO_4)_4,24H_2O$; $HBr,5H_2O$; $KClO_3,2H_2O$; $BaCl_2,4H_2O$, and others; the latter in that of ferrous, copper, zinc, magnesium, and manganese sulphates. In the case of the monohydrate of sulphuric acid, H_2SO_4,H_2O, the molecule of water has a density of $\frac{4}{3}$; the second molecule existing in the hydrate $H_2SO_4,2H_2O$ has a density of $\frac{6}{5}$.

The density of an aqueous solution of a salt is dependent on the following factors:—(1) the quantity of anhydrous salt in solution; (2) the quantity of the combined water; (3) the quantity of uncombined water having a density 1. Knowing the density of the anhydrous salt, and which of the expressions $\frac{6}{5}$ and $\frac{4}{3}$ represents the density of the combined water, the density of an aqueous solution of any strength can be readily calculated. The paper contains a series of tables, which show how very closely the numbers obtained by such calculations agree with those found by observation. G. T. M.

Action of Arseniuretted Hydrogen on Potassium Permanganate. By D. TIVOLI (*Gazzetta*, **19**, 630—632).—When a current of pure arseniuretted hydrogen is passed into a dilute solution of potassium permanganate, a brown precipitate is formed, the liquid after a time becoming clear and colourless. The following reactions take place:—(1) $AsH_3 + 2KMnO_4 = K_2HAsO_4 + Mn_2O_3 + H_2O$; (2) $AsH_3 + 2KMnO_4 = K_2HAsO_3 + 2MnO_2 + H_2O$. The first reaction is the principal one, the solution containing potassium arsenate and only small quantities of arsenite; part of the arsenate is mechanically retained by the precipitate. The latter consists of hydrated sesquioxide of manganese mixed with small and variable quantities of the hydrated peroxide. S. B. A. A.

Note on the Diamond. By A. KRAUSE (*Ber.*, **23**, 2409—2412).—Diamond splinters were burnt in a current of oxygen, the products of combustion absorbed by ammonia, and the ammoniacal solution decomposed with pure sodium hydroxide. A comparison of the crystals obtained on evaporation with those of pure sodium carbonate, showed that they had the same percentage of water of crystallisation, and that they were identical in crystalline form, optical properties, melting point, electrical conductivity, and solubility in water. The author concludes that the diamond must be chemically identical with carbon, since not only is the atomic weight the same, but on oxidation they both yield exactly the same product. J. B. T.

Potassium Tetrathionate and Pentathionate. By A. FOCK and K. KLÜSS (*Ber.*, **23**, 2428—2432).—The authors have examined the crystals to which Rammelsberg gave the formula $K_2S_5O_6$, and find them to be really potassium tetrathionate, $K_2S_4O_6$, and they suggest that the analysis which Rammelsberg published was made with a different and impure preparation. The compounds described by Lewis (Trans., 1881, 68, and 1882, 300) and Shaw (Trans., 1883,

357) are really potassium pentathionate, $2K_2S_5O_6 + 3H_2O$, not $K_2S_5O_6 + H_2O$, as the latter states; there is therefore only *one* potassium pentathionate. Potassium tetrathionate crystallises in peculiar hemimorphous or hemihedral forms belonging to the monosymmetric system, not to the rhombic system as stated in Shaw's paper. Potassium pentathionate crystallises in thick prisms and in flat plates, both forms belonging to the rhombic system. J. B. T.

Copper Oxysulphides. By T. CLICHE (*Arch. Pharm.*, **228**, 374—414).—The action of ammoniacal copper oxide solution on cupric sulphide when hot, as in the volumetric estimation of copper by (standard) sodium sulphide solution, does not add oxygen to the sulphide, but removes sulphur; the sulphide is partially or completely converted into cuprous sulphide, and the conversion is the more complete the higher the temperature and the more concentrated the oxide solution; both temperature and state of concentration affect the result in a marked manner. The cuprous sulphide is not further attacked. The sulphur removed is oxidised to sulphuric acid, whilst the cupric oxide in solution is reduced to cuprous oxide; the filtrate consequently always contains sulphuric acid when the cupric oxide solution has been prepared either from chloride, nitrate, or acetate. In neutral or acid solutions, the same reaction takes place, but the oxide does not yield up oxygen; the copper solution only acts as a carrier of oxygen from the air. The products of the action of the oxide solution on the sulphide are not oxysulphides, but compounds or mixtures of cupric and cuprous sulphide, and sulphate is always present, due to the easy oxidation of the cupric sulphide, except in the case when cuprous sulphide alone is formed. The water of crystallisation and the combined oxygen of the sulphate are reckoned as oxygen; the compound is considered to be an oxysulphide. The action of concentrated sulphuric acid on metallic copper yields sulphurous anhydride and cupric sulphate, but does not produce oxysulphide, but only cuprous sulphide, so long as any metallic copper is present. This sulphide first appears brown, and then black; it does not oxidise in the air, or only very slightly. When the whole of the metallic copper has dissolved, cupric sulphide is produced by the action of sulphuric acid on the cuprous sulphide, and the newly formed compound is attacked in turn with the separation of free sulphur, the two reactions proceeding simultaneously. The sulphur thus set free is insoluble in carbon bisulphide, and can reproduce cupric sulphide on heating cuprous sulphide with it. J. T.

New Ammoniacal Mercury Compounds, and a New Reaction for Mercurammonium Compounds. By L. PESCI (*Gazzetta*, **19**, 509—526).—On adding ammonia to a solution of mercuric bromide, a flocculent, light-yellow precipitate is slowly formed; this substance is probably analogous to "infusible white precipitate," Hg_2NCl,NH_4Cl, but its composition cannot be definitely ascertained, as it continually loses ammonium bromide when washed with cold water. By treatment with boiling water, it becomes orange-yellow, loses bromine, and its composition gradually approximates to Hg_2NBr.

When an aqueous solution of mercuric bromide is treated with excess of ammonium carbonate, a heavy, white precipitate of needles is formed which readily loses ammonium bromide when treated with water, being converted into the preceding yellow compound. When treated with warm potash or soda, it loses ammonia, and is transformed into mercurammonium bromide, Hg_2NBr. After purification by washing with a dilute solution of ammonium carbonate and drying over sulphuric acid, its composition was $4Hg_2NBr,5NH_4Br$. It is readily soluble in cold hydrochloric acid, but is insoluble in nitric acid; it dissolves in warm, dilute, sulphuric acid (10 per cent.), but mercuric bromide crystallises out on cooling; it also dissolves in ammonium chloride, bromide, or iodide with evolution of ammonia. At an elevated temperature, it decomposes without melting.

Mercurammonium bromide, Hg_2NBr, obtained by the decomposition of the preceding compound with potash or soda, or by treating Millon's base with dilute hydrobromic acid, is a pale, orange-yellow, anhydrous powder readily soluble in dilute hydrochloric acid, but insoluble in water and in nitric or sulphuric acids. It behaves like the preceding compound with ammonium chloride, bromide, or iodide. It decomposes on heating without previous fusion, giving off small quantities of ammonia, and forming a sublimate consisting principally of metallic mercury.

When either mercurammonium bromide or the compound $4Hg_2NBr,5NH_4Br$ is treated with a boiling solution of ammonium bromide and filtered after a short contact, the filtrate deposits, on cooling, colourless, microscopic crystals of the composition $Hg_2NBr,3NH_4Br$. The same compound is obtained on adding dilute ammonia to a solution of mercuric bromide in ammonium bromide, or by mixing alcoholic solutions of mercuric bromide and ammonia; in the latter case, however, the product is amorphous. It is decomposed by water, but not by alcohol. It melts at 180° with evolution of ammonia, whilst at a higher temperature a white powder and drops of a yellow liquid are sublimed. It is readily soluble in hydrochloric acid; it also dissolves in hot dilute sulphuric acid, but mercuric bromide separates on cooling; it slowly dissolves in ammonium chloride, bromide, or iodide with evolution of ammonia. It is decomposed by potash or soda with the formation of mercurammonium bromide and ammonia.

The presence of the mercurammonium radicle, Hg_2N, may generally be ascertained by the resistance of its salts to the action of potash or soda and by their decomposition by sodium sulphide; in double salts of mercurammonium and ammonium, the ammonium salt is split off and decomposed by alkalis, and the mercurammonium salt may then be detected by sodium sulphide. As, however, some double salts of mercury and ammonium (for example, $HgCl_2,NH_4Cl$, $HgCl_2,2NH_4Cl$, $HgCl_2,2NH_4I$, &c.) are converted into mercurammonium compounds by treatment with alkalis, the presence of the radicle in the original compound cannot always be determined by this method.

The evolution of ammonia by mercurammonium compounds when treated with ammonium bromide affords a ready means of detecting

the radicle; the ammonia may be quantitatively determined by allowing the reaction to proceed for about 48 hours in a closed bell-jar in presence of a definite quantity of oxalic acid. When neutral mercurammonium salts are treated in this way, one-fourth of the evolved ammonia proceeds from the radicle, the reaction which takes place being represented by the equation $Hg_2NX + 3NH_4X = 2HgX_2 + 4NH_3$. The residual solution contains a double salt of mercury and ammonia, which is reconverted into a mercurammonium salt on the addition of ammonia. S. B. A. A.

Cobalt and Nickel Oxides. By G. SCHRÖDER (*Chem. Centr.*, 1890, i, 931—932, *Inaugural Dissertation*).—The author finds that if the cobalt oxide, Co_3O_5, obtained by treating a solution of a cobalt salt with potassium hypochlorite or hypobromite, is heated to boiling in the liquid, oxides varying in composition from Co_3O_5 to Co_2O_3 are formed, and that the same oxides are produced if the solution of the cobalt salt is first treated with bromine and then with potassium hydroxide.

Since the higher oxide, Co_3O_5, is more readily washed than the cobaltic oxide, Co_2O_3, it is recommended to precipitate cobalt as the higher oxide for the purpose of quantitative analysis. If solutions of salts of nickel are treated in the manner described above, nickel oxide, Ni_2O_3, is the only product. If, on the other hand, potassium hydroxide and, afterwards, bromine are added to the nickel solution, a lower oxide, Ni_5O_7, having a formula between Ni_2O_3 and NiO, is formed. The oxides Ni_5O_7, Ni_2O_3 lose oxygen when boiled in potash solution, and form oxides of an indefinite constitution. J. W. L.

Constitution of the Cobalt, Chromium, and Rhodium Bases. By S. M. JÖRGENSEN (*J. pr. Chem.* [2], **42**, 206—221).—The compound described by Fremy and Cleve as chlorotetraminechromic chloride, $(Cr,4NH_3)Cl_3,H_2O$, is best prepared in the manner previously described by the author (Abstr., 1880, 10). To the mixed solution of chlorotetramine- and chloropurpureo-chromic chloride obtained as there stated, ammonium sulphate is added, the precipitated chlorotetraminechromic sulphate washed with water, and reconverted into the chloride by mixing with moderately concentrated hydrochloric acid. To free this compound from sulphuric acid, it is dissolved in water and filtered, and the filtrate allowed to fall into moderately concentrated hydrochloric acid. Its molecular weight, found by Raoult's method, agrees, as previously stated (this vol., p. 953), with the simple empirical formula given above. In its general behaviour, it strongly resembles the purpureo-compounds, and it is therefore probable that, as in these compounds, one of the chlorine-atoms is combined with the metal. That this is really the case is shown by the fact that only two-thirds of the chlorine is immediately precipitated by silver nitrate in candle light. The composition of the salts described below is also in agreement with this supposition, as is also the fact that the platinochloride contains only one atom of platinum for every chlorine-atom in the molecule.

Chlorotetraminechromic nitrate, $Cl(Cr,4NH_3)2NO_3,H_2O$, is prepared

by the addition of nitric acid to a solution of the chloride. It is a beautiful, almost carmine-red salt, and at 100° undergoes a remarkable change, assuming a deep-black colour, and dissolving in water forming a bluish-black solution. In this it differs from the otherwise similar chloropurpureochromic nitrate. The corresponding *bromide*, $Cl(Cr,4NH_3)Br_2,H_2O$, is a violet-red precipitate.

A cobaltammonium chloride of similar composition has been also obtained by Vortmann (Abstr., 1883, 25, this vol., p. 14), and a careful comparison of both compounds has shown that they closely correspond with one another in all their properties, and the author, therefore, terms Vortmann's compound *chlorotetraminecobalt chloride*, $Cl(Co,4NH_3,H_2O)Cl_2$. It was prepared according to the method given by Vortmann, and purified in a manner similar to that given for the chromium salt. It forms a violet, crystalline powder, scarcely distinguishable from chloropurpureocobalt chloride, and soluble in 40 parts of water at the ordinary temperature. Its molecular weight, as found by Raoult's method, agrees with the formula given above. Silver nitrate only precipitates two-thirds of the chlorine in the cold, and sulphuric acid drives off two-thirds of the chlorine as hydrogen chloride, forming the *sulphate* $Cl(Co,4NH_3,H_2O)SO_4$, which crystallises in rhombic tablets, and is isomorphous with the corresponding chromium salt. The *platinochloride*, $Cl(Co,4NH_3,H_2O)PtCl_6,2H_2O$, only contains one atom of platinum for every atom of chlorine present, and crystallises in brown needles which have a silky lustre, and lose their water of crystallisation at 100° or over sulphuric acid. The *bromide*, $Cl(Co,4NH_3,H_2O)Br_2$, is a bluish-violet, crystalline precipitate more soluble than the chloride. The *chromate*, $Cl(Co,4NH_3,H_2O)CrO_4$, forms a greenish-brown precipitate, soluble in cold water with an olive-green colour.

The foregoing description shows that these two chlorotetramine-salts correspond in their composition and general properties with the chloropurpureo-salts, but differ from them in containing $1H_2O$ in place of $1 NH_3$.

$Cl(Cr,4NH_3,H_2O)Cl_2$.	$Cl(Co,4NH_3,H_2O)Cl_2$.
$Cl(Cr,4NH_3,NH_3)Cl_2$.	$Cl(Co,4NH_3,NH_3)Cl_2$.

The chlorides of both series are isomorphous, and appear to have approximately the same molecular volume. The characteristic fluosilicates of these compounds also form crystals, the difference in the angles of which is very slight. There can, therefore, be no doubt that the first series contain a bivalent radicle isomeric with water in place of NH_3. In confirmation of this it is found that when chlorotetraminecobalt chloride is heated on the water-bath, first with ammonia and then with an excess of hydrochloric acid, it is converted into chloropurpureocobalt chloride. On the other hand, the latter compound, when treated with silver carbonate, yields the roseochloride, the solution of which is converted, on evaporation on the water-bath, into chlorotetraminecobalt chloride. Vortmann has shown that the latter readily passes into the praseochloride, and *vice versâ*.

For the tetramine salts, the author proposes the constitutional

formula $R'''\begin{cases}Cl\\ OH_2\cdot Cl\\ NH_3\cdot NH_3\cdot NH_3\cdot NH_3\cdot Cl\end{cases}$, corresponding with those already given for the chloropurpureo- and chloropraseo-salts (*J. pr. Chem.* [2], **41**, 437). The formation of these salts also emphasises the author's previous statement that one of the NH_3-groups in the purpureo-salts is less firmly combined than the remaining four.

H. G. C.

Cryoscopic Investigations of Colloïds. By A. Sabanéeff (*J. Russ. Chem. Soc.*, **21**, 515—525).—The author has studied the application to some colloïdal substances of Raoult's method of determining the molecular weight from the depression of the freezing point.

Colloïdal tungstic acid was prepared by Graham's method by dialysing a weak hydrochloric acid solution of sodium tungstate. On evaporating the dialysed solution on the water-bath or in a vacuum over sulphuric acid, an amorphous, transparent snbstance was obtained, the composition of which, after dryiug at 200°, corresponded with the formula $3WO_3,H_2O$. The depression was identical for both kinds of preparations. The numbers obtained with solutions containing 1·2—100 parts of the acid in 100 parts of water varied from 0·035—1·910°, from which the value 679—995 was calculated as the molecular weight, that of $3WO_3,H_2O$ being = 714. Colloïdal tungstic acid is therefore tritungstic acid.

Colloïdal molybdic acid was prepared in the same manner as the foregoing. After evaporation of the dialysed solution in a vacuum over sulphuric acid, it is left as transparent, hygroscopic, gum-like crusts, soluble in water without change, but on heating the solution a white precipitate separates, and on evaporating to dryness an insoluble residue is left. Immediately after preparation, the salt contains 11·2 per cent. of water; after drying for several weeks over sulphuric acid, only 6·92 per cent. With the time of drying, the solubility of molybdic acid in water is found to decrease, and after some time it becomes insoluble. The depression of the freezing point for solutions containing 1·6—5·1 parts in 100 parts of water gives M = 608—631, the number calculated for $(MO_3)_4$ being 576.

Glycogen.—A very pure preparation was used. For solutions containing 4·06—8·29 parts in 100 parts of water, a depression of 0·050—0·095 was found, giving M = 1545—1625. The molecular weight $(C_6H_{10}O_5)_{10}$ = 1620. The effect of fermentation of glycogen shows that the molecule must be double, $C_6H_{10}O_5$, whilst the action of dilute sulphuric acid (Shtcherbakoff) shows that its true formula is five times larger than the empirical one. On heating at 115°, glycogen loses 3·58 per cent. of its weight, and on dissolving the residue in water and determining the depression of the freezing point, values were obtained for the molecular formula which are $1\frac{1}{2}$ times smaller than the above, pointing probably to the existence of several modifications.

Silicic Acid.—On dialysing a weak solution of hydrochloric acid to which one of pure sodium silicate was added, solutions containing up to 37 per cent. of silicic acid were obtained by boiling down the solution in a flask, whereas the solution of maximum concentration obtained by Graham's method, containing 14 per cent., was found to be very

unstable. The depression of the freezing point of solutions, purified by repeated addition of hydrochloric acid and dialysis, was found to be about 0·002°, that is, smaller than the possible experimental error. It shows that the molecular weight of silica is extremely high. Assuming that the depression lies between 0·005° and 0·0025°, and that silica is a polymeride, $(SiO_2)_n$, the value of n will lie between 800 and 1600.

Colloïdal Ferric Hydrate.—On dialysing a solution of pure ferric hydroxide in a small quantity of hydrochloric acid, a solution is obtained, containing, even after weeks, some hydrochloric acid. The purest preparations obtained in this way were found to correspond with the composition $Fe_2Cl_6,116Fe_2(OH)_6$. The freezing-point depression of solutions containing $16Fe_2(OH)_6$ for $1Fe_2Cl_6$ was found to be 0·065°, and with increasing number of molecules of hydroxide, the depression was found to diminish, as shown in a tabular arrangement, down to the proportion $Fe_2Cl_6,116Fe_2(OH)_6$, when it was found to be inappreciable. From this it follows, that the hydroxide alone causes no depression, but that the effect is due to the chloride only, and that the molecular weight of the hydroxide in solution is extremely large. On assuming, therefore, that the depression is due only to the presence of the chloride, and recalculating the values accordingly, values were obtained for the molecular weight of the chloride varying between 270 and 342. The molecular weight of $Fe_2Cl_6 = 325$. The depression of 1 gram of substance in 100 parts of water for ferric chloride is, according to Raoult, = 0·356°, therefore six times larger than the normal value, 0·0584°, obtained by the author. Raoult's large value is due to a dissociation of ferric chloride in aqueous solution, and in the above case, in the presence of a large amount of ferric hydroxide, that is, one of the products of dissociation, scarcely any dissociation takes place. It is interesting to note that the electrical conductivity decreases with the decreasing amount of ferric chloride present, so that the author concludes that pure ferric hydroxide in aqueous solution does not conduct.

Egg albumin, purified by Michailoff's method, shows, in aqueous solution, an appreciable lowering of temperature. A solution of 15·6 parts in 100 parts of water shows a depression of 0·02°, from which it follows that the molecular weight is about 15,000.

Referring to Lubavin's experiments (this vol., p. 685), the author has subjected his solutions to the temperature of −20° for at least one hour, until they became perfectly solid. No coagulation of tungstic or molybdic acid, of glycogen, or albumin occurred, and complete solution took place after fusion. A solution of silica treated in the same manner yielded the greater part of the silica in the insoluble state. The author concludes by remarking that his experiments were carried out before the publication of the interesting researches of Morris and Brown.

B. B.

Composition of Some Metallic Sulphides obtained in the Wet Way, and Reactions of the Sulphide of Gold, Au_2S_2. By W. ANTONY and A. LUCCHESI (*Gazzetta*, 19, 545—562).—To decide whether lead, copper, bismuth, antimony, and gold are precipitated

from their solutions by sulphuretted hydrogen as sulphides, or as hydrosulphides, a series of experiments were made, the filtration being conducted under a bell jar, through which a current of hydrogen sulphide was continually passing; boiled water saturated with the gas was used for washing, and was brought on to the precipitate by means of a tube passing through the stopper of the bell jar. The washed precipitate was quickly pressed between filter paper and dried in a current of perfectly pure nitrogen, the temperature being gradually raised to 120—130°, and the issuing gas led through a solution of silver nitrate; the dried sulphide was then analysed. Under these circumstances, the lead precipitate has the composition PbS, the bismuth precipitate, Bi_2S_3; the precipitate from tartar emetic is Sb_2S_3, and that obtained by adding excess of hydrochloric acid to a freshly prepared solution of sodium thioantimonate is Sb_2S_5; the copper precipitate obtained at the ordinary temperature could not be properly washed in the apparatus, but when prepared at 0°, and washed by decantation with sulphuretted hydrogen water at 0° until the precipitate was sufficiently compact for treatment, its composition was found to be CuS.

Dilute solutions of gold (1 per cent.) treated at 90—100° with a current of hydrogen sulphide give a precipitate of pure gold; dilute solutions (1—3 per cent.) treated in the same way at the ordinary temperature (about 8°) yield a black precipitate of Au_2S_2. The temperature of the solution continually rises during the precipitation proportionately to the strength of the solution, and if at any time the temperature approaches 40°, metallic gold is precipitated along with the sulphide. If the solution is not fully precipitated, and the sulphide is allowed to remain in contact with the solution of auric chloride, these salts react according to the equation $4AuCl_3 + 2Au_2S_2 + 8H_2O = 6Au + 12HCl + 2H_2SO_4$, metallic gold being formed. From solutions of aurous sodium thiosulphate, hydrogen sulphide precipitates mixtures of gold, sulphur, and aurous sulphide, which always vary in composition; the action of auric chloride on these solutions is as described by Fordos and Gélis (*Ann. Chim. Pharm.* [3], **13**, 394), the liquid being at first coloured reddish-brown, owing to the formation of a soluble compound rich in gold; but after adding a few drops of the reagent, a precipitate of Au_2S_2 is formed; this is again decomposed by an excess of auric chloride, in accordance with the equation given. When auric chloride is added to potassium or sodium hydrosulphides, Au_2S_2 is formed, and dissolves in excess of the reagent; with ammonium hydrosulphide, however, the precipitate of Au_2S_2 at first formed is immediately deprived of its sulphur and reduced to metallic gold. When aurous sulphide is left in contact with either colourless or yellow ammonium sulphide, it is similarly reduced.

S. B. A. A.

A New Anhydrous Double Chloride of Gold and Potassium. By A. LAINER (*Monatsh.*, 11, 220—223).—The author has obtained a compound having the formula $AuCl_3,KCl$, by dissolving gold in aqua-regia, and adding the molecular proportion of potassium chloride dissolved in a little water. After sufficient concentration of the

solution over quick-lime and over sulphuric acid, crystallisation commenced, and a deposit of glistening, yellow needles was obtained, which remained unchanged on exposure to the air. The crystallographic measurements of these needles correspond exactly with those of crystals obtained by Topsöe (*Monatsh.*, 1874, 265), and to which he attributed the formula $2(AuCl_3,KCl) + H_2O$. G. T. M.

Platososemiamine Chloride, an Isomeride of Magnus' Salt. By A. Cossa (*Ber.*, **23**, 2503—2509).—By the action of a boiling solution of ammonium nitrate on Magnus' salt a mixture is obtained, consisting of platosamine chloride, platinodiamine chloronitrate (Gros), and a compound isomeric with Magnus' salt. It is insoluble in alcohol; 100 parts of water dissolve 0·34 part at 17°, and 1·82 parts at 100°; it crystallises from water in yellow, lustrous plates, of sp. gr. 3·61. On boiling with excess of ammonia, platosodiamine chloride is formed, whilst with oxidising agents it yields platinodiamine chloride. The author regards the substance as a compound of 1 mol. of platosodiamine chloride and 2 mols. of the chloride of a new base (platinosemiamine) $PtCl{\cdot}NH_3Cl$. The *potassiochloride* of this base, $Pt(NH_3)Cl_2,KCl,H_2O$, is readily soluble in water, and yields the isomeride of Magnus' salt on treatment with platosodiamine chloride. The isomeride is also formed by the addition of ammonia to platinous chloride, and by its elimination from platososemiamine chloride. J. B. T.

Organic Chemistry.

Geometrical Isomerism of the Bromo-derivatives of Pseudobutylene. By A. Favorsky and C. Debout (*J. pr. Chem.* [2], **42**, 149—155).—In this paper the authors show that Wislicenus and Hölz, in their work on the brominated derivatives of pseudobutylene (Abstr., 1889, 576), were dealing with a mixture of butylenes, and therefore with a mixture of derivatives, not with geometrical isomerides. Their theoretical conclusions, consequently, are unsound. A. G. B.

Hexadecylene Bromide Derivatives. By F. Krafft and L. Grosjean (*Ber.*, **23**, 2352—2356).—Pure hexadecylene bromide is prepared by treating a carbon bisulphide solution of pure hexadecylene with the calculated quantity of bromine dissolved in the same medium; the partially purified hydrocarbon from spermaceti may also be emyloyed. The bromide boils at 225—227° at 15 mm. without decomposition. *Diacetylhexadecylene*, $C_{16}H_{32}(OAc)_2$, is obtained by boiling pure hexadecylene bromide with glacial acetic acid for 5—6 hours, the excess of acid is evaporated under reduced pressure, the residue dissolved in alcohol, and precipitated

with water; it crystallises in colourless plates, melting at 55—56°. *Hexadecylene glycol*, $C_{16}H_{31}(OH)_2$, is prepared by boiling the diacetyl-derivative with alcoholic potash; the product is poured into cold water, and the precipitated glycol purified by re-crystallisation from alcohol; it melts at 72—73°, and, in small quantities, boils unchanged at 210—211° under a pressure of 9 mm., and 220—221° at 15 mm. *Hexadecylenedicarboxylic anhydride*, $C_{18}H_{32}O_3$, is formed by treating hexadecylene bromide with potassium cyanide, and hydrolysing the product with alcoholic potash; it melts at 73—75°, and boils at 245—248° at 15 mm. *Hexadecylenedicarboxylic acid*, $C_{16}H_{32}(CO\cdot OH)_2$, is obtained by dissolving the anhydride in dilute ammonia, and precipitating with dilute hydrochloric acid; it melts at 121°, and is converted into the anhydride. The *silver salt* is crystalline. J. B. T.

The Two Diiodides of Acetylene. By E. PATERNÒ and A. PERATONER (*Gazzetta* **19**, 580—601).—The existence of two isomeric symmetrical diiodoethylenes, CHI:CHI, is a point of some importance in the theory of isomerism in space, and has hitherto been taken as established by Sabanéeff's experiments (*Annalen*, **178**, 122); the authors have now re-investigated the subject. By passing acetylene over iodine in presence of absolute alcohol with frequent agitation, Sabanéeff obtained a solid iodide crystallising in needles, melting at 73°, and boiling at 192°, a liquid compound solidifying below 0°, and a small quantity of another very volatile iodide. On repeating these experiments, the authors obtained a large quantity of the solid iodide together with a very small quantity of an impure liquid product. When the reaction takes place in an acetic acid solution (instead of in alcohol), nothing but the solid iodide is formed; on the other hand, in presence of an excess of iodic acid, the product consists mainly of the liquid iodide, a small quantity of moniodacetylene, C_2HI, being also formed; the latter is also obtained in minute quantities in the other methods of preparing the iodides. The iodide is a heavy liquid with a pleasant, ethereal odour, boils at 29—32°, and does not solidify in a mixture of ice and salt. On heating it in a closed vessel above its boiling point, it decomposes with a slight explosion into carbon and hydrogen iodide. It combines with cuprous chloride forming a red, flocculent compound analogous to copper acetylide. In an acetic acid solution, it readily combines with hydriodic acid to form the solid diiodide; this crystallises in large colourless needles which cannot be powdered on account of their ductility. It melts at 71° and volatilises in a current of steam, but, contrary to Plimpton's statement (Trans., 1882, 392), it is largely decomposed when distilled under the ordinary pressure.

The liquid iodide cannot be obtained pure on account of its instability; the analyses are very discrepant but point towards a formula $C_4H_4I_2$; the crude product is always discoloured by iodine, and when decolorised by washing with potash it soon turns yellow or reddish-brown again. It has a pleasant odour recalling that of violets; it is insoluble in water, but dissolves in alcohol, ether, benzene, and acetic acid; it is an excellent solvent for the solid iodide. It undergoes

some change when merely heated on the water-bath; it boils with decomposition at 160—165°, and is converted into the solid iodide by distillation in a current of steam under reduced pressure; when heated for several hours with water in a reflux apparatus, the products consist of the solid iodide, iodine, and hydriodic acid. It does not solidify at a few degrees below 0° as affirmed by Sabanéeff, but remains liquid even at −18°. Sabanéeff's liquid iodide appears to have been a solution of the solid in the liquid iodide.

When the solid iodide is heated with mercuric chloride (2 parts) and alcohol at 180—190° for 8—10 hours, and the product is steam-distilled, acetylene chloriodide, CH_2ICl, passes over; mercuric chloride acts much more readily on the liquid iodide, the same product being formed; a portion of the iodide is, however, decomposed during the reaction. Iodine chloride acts similarly on both the iodides forming the same chloriodide, CHCl⁚CHI. By treatment with benzene and aluminium chloride, anthracene is formed together with a hydrocarbon which distils between 250° and 290°, yields benzoic acid on oxidation with potassium permanganate, and probably has the composition $C_2H_4Ph_2$.

The analogies between the above results and those obtained by Demole (Abstr., 1880, 158), Anschütz (Abstr., 1887, 150) and Heppe (Abstr., 1875, 361) render the formula CHI⁚CHI a more probable one for the iodides than CH_2⁚CI_2. Silver acetate has no action on the solid iodide, but forms a monacetate with the liquid compound. Both iodides deposit iodine when heated with alcohol and iodic acid, although no moniodacetylene appears to be formed. From the foregoing experiments it would seem that the first product of the action of acetylene on iodine is the liquid iodide, of which the products of decomposition (C_2HI and HI) combine to form the symmetrical solid iodide, CHI⁚CHI; a portion of the iodine, however, acts directly on acetylene forming the moniodo-derivative. Although the liquid iodide behaves as a symmetrical diiodide of acetylene, and is capable of almost complete transformation into the solid compound, it appears to have the composition $C_2H_2I_2 + C_2H_2$. The existence of two different isomeric symmetrical diiodoethylenes is therefore still unproved. S. B. A. A.

Dimethylacetylene and its Tetrabromides. By A. Favorsky (*J. pr. Chem.* [2], **42**, 143—149).—The author has already shown (*J. pr. Chem.* [2], **37**, 383, 430) that by the action of alcoholic potash on monosubstituted ethylacetylene, a hydrocarbon, C_4H_6, is obtained, having the properties of dimethylacetylene and yielding hexamethylbenzene on treatment with sulphuric acid.

A dibromide, $C_4H_6Br_2$, is obtained as a yellow oil by brominating an ethereal solution of this hydrocarbon at a low temperature. By further bromination (equal mols.) at the ordinary temperature, a crystalline tetrabromide is obtained; when this is recrystallised at the ordinary temperature, the crystals retain their transparency and lustre for some time, whereas when it is recrystalised at a low temperature, the crystals quickly become opaque and milky, especially when touched with one of the first mentioned crystals. Both kinds

melt at 230° with some decomposition; their crystallography is fully given.

None of the hydrocarbons of the formula C_4H_6, except Henninger's erythrene, identical with Ciamician and Magnanini's pyrrolylene, have been isolated, being only known as their tetrabromides. The proximity of the melting points of these tetrabomides to that of erythrene tetrabromide indicates the probability of their identity with it. A. G. B.

γ-Chlorobutyronitrile. By S. GABRIEL (*Ber.*, **23**, 2489—2493; compare preceding abstract).—With the hope of throwing light on some of the reactions of orthocyanobenzyl chloride, the analogous fatty compound, γ-chlorobutyronitrile, $CN\cdot CH_2\cdot CH_2\cdot CH_2Cl$, has been investigated. *γ-Thiocyanobutyronitrile*, $CN\cdot[CH_2]_3\cdot SCN$, is prepared by boiling γ-chlorobutyronitrile with alcoholic potassium thiocyanate for two hours in a reflux apparatus; the alcohol is evaporated, the residue treated with water, and the oily portion separated. It is a pale-yellow, almost odourless liquid, boiling at 195° under a pressure of 30—40 mm., and 220° at 110—120 mm.; it undergoes slight decomposition on distillation at the ordinary pressure. *γ-Dithiodibutyramide*, $NH_2\cdot CO\cdot[CH_2]_3\cdot S\cdot S\cdot[CH_2]_3\cdot CO\cdot NH_2$, is obtained by treating the previous compound with concentrated sulphuric acid in the cold; the reaction is violent, a considerable evolution of carbonic and sulphurous anhydrides taking place. After remaining over night, the liquid is poured into cold water, treated with a slight excess of ammonia, and evaporated; on recrystallisation from water, it is deposited in flat needles which melt at 166—167°.

The reaction probably proceeds in two stages; by the elimination of ammonia and carbonic anhydride, an intermediate mercaptan-derivative, $NH_2\cdot CO\cdot[CH_2]_3\cdot SH$, is probably formed, from which hydrogen is eliminated by the action of sulphuric anhydride. *γ-Dithiodibutyric acid*, $COOH\cdot[CH_2]_3\cdot S_2\cdot[CH_2]_3\cdot COOH$, is obtained on boiling the amide with concentrated hydrochloric acid; it crystallises from water in plates melting at 108—109°, and is readily soluble in ammonia and alkalis. On heating γ-chlorobutyronitrile with excess of alcoholic hydrogen potassium sulphide for $\frac{1}{2}$—1 hour, crystals are formed; after washing these with alcohol and water, vermilion-red needles are obtained melting at 113—114°. The compound is soluble in alcohol and benzene, but insoluble in water; it has the formula $C_8H_{10}S_3$, and is the analogue of the compound $C_{16}H_{10}S_3$, from orthocyanobenzyl chloride (*loc. cit.*). The *methiodide*, $C_8H_{10}S_3,MeI$, is prepared by dissolving the compound in methyl iodide: on recrystallisation from alcohol, it melts at 103—104°. The formation of this iodide appears to indicate that the red compound is a sulphide of the series R_3S, and its constitution may, perhaps, therefore be represented by the formula $S(C_4H_5S)_2$.

γ-Thiodibutyronitrile, $S(C_3H_6\cdot CN)_2$, is obtained on warming γ-chlorobutyronitrile with alcoholic potassium sulphide; it is a colourless, oily liquid boiling above 300°, and is almost odourless at ordinary temperatures. With concentrated hydrochloric acid, it yields *γ-thiodibutyric acid*, $S(C_3H_6\cdot COOH)_2$, which is deposited from water in long,

flat crystals melting at 99°. It is readily soluble in ammonia and fixed alkalis. J. B. T.

Constitution of the Derivatives of Cyanamide. By A. SMOLKA (*Monatsh.*, 11, 179—219; compare Abstr., 1888, 42 and 830; 1889, 114 and 951).—The author has fully and carefully reviewed the syntheses and reactions of substituted cyano-compounds, with the object of proving their derivation and constitution. Tables are appended showing the constitution of the possible compounds which may be regarded as being derived (1) from cyanamide, $CN{\cdot}NH_2$, dicyanodiamide, $CN{\cdot}NH{\cdot}C(NH){\cdot}NH_2$, carbamidocyanamide, $CN{\cdot}NH{\cdot}CO{\cdot}NH_2$, and thiocarbamidocyanamide, $CN{\cdot}NH{\cdot}CS{\cdot}NH_2$, by the addition of the elements of ammonia, water, and hydrogen sulphide respectively; (2) from cyanamide, by the addition of another molecule of cyanamide, cyanic and thiocyanic acids respectively; (3) from cyanamide or guanidine, cyanic acid or carbamide, thiocyanic acid or thiocarbamide, by combination with guanidine, carbamide and thiocarbamide respectively; and (4) from dicyanodiamide or biguanide, amidodicyanic acid or dicyanodiamidine (guanyl carbamide), thiocarbamincyamide or thiodicyanodiamidine, biuret, thiobiuret, and dithiobiuret, by combination with cyanamide or guanidine, cyanic acid or carbamide, thiocyanic acid or thiocarbamide respectively. It would be possible to synthesise all the compounds appearing on the tables, if the uret, biuret, triuret, and dicyanodiamide compounds known have the constitutions there attributed to them. Many of the syntheses have been actually brought about; others, however, are impracticable, owing to the compounds being themselves unstable under the conditions necessary to induce combination between their generators. G. T. M.

Crystallisation of Sodium Hydroxide from Isobutyl Alcohol. By C. GÖTTIG (*Ber.*, 23, 2246—2247).—A compound of the composition $NaOH,6C_4H_{10}O$, is deposited in well-defined crystals, when an almost saturated solution of sodium hydroxide in isobutyl alcohol is evaporated over sulphuric acid; when placed on water, it behaves like other compounds of the same nature, and moves about the surface very quickly during solution. The crystals lose 5 mols. of the alcohol over sulphuric acid. F. S. K.

Oxidation of δ-Methylethylethylene Glycol. By H. v. PECHMANN (*Ber.*, 23, 2427—2428).—δ-Methylethylethylene glycol, $OH{\cdot}CHMe{\cdot}CHEt{\cdot}OH$, is treated with bromine-water (4 atomic proportions) and exposed to direct sunlight for a day; the solution is decolorised with sulphurous anhydride, sodium chloride is added, and the solution distilled. The distillate contains acetylpropionyl, and on treatment with phenylhydrazine, the osazone (m. p. 166—167°) is obtained. Certain other compounds, such as hydrobenzoïn and tartaric acid, which contain a secondary glycol-group, may be oxidised in the same manner, but diisopropyl glycol is not converted into the corresponding diketone in this way. J. B. T.

Syntheses in the Sugar Group. By E. FISCHER (*Ber.*, **23**, 2114—2141).—The present paper is a brief survey of the results which have been obtained by the author and others in their investigations of the sugar group.

A few years ago (1886), dextrose, levulose, galactose, and sorbinose were the simplest known members of the sugar group, arabinose, which was at one time thought to be an isomeride of grape-sugar, having been shown by Kiliani (Abstr., 1887, 465) to have the molecular formula $C_5H_{10}O_5$.

The constitution of dextrose and galactose is, at the present time, expressed by the formula $CH_2(OH)\cdot[CH(OH)]_4\cdot COH$, and that of levulose by the formula $CH_2(OH)\cdot[CH(OH)]_3\cdot CO\cdot CH_2\cdot OH$, these formulæ being based on the following facts:—On reduction with sodium amalgam, dextrose and levulose yield mannitol, and galactose yields dulcitol, both of which compounds were proved to be hexahydric derivatives of normal hexane. On oxidation with chlorine- or bromine-water, dextrose and galactose are converted into monocarboxylic acids, gluconic acid and galactonic acid, and on further oxidation into dicarboxylic acids, saccharic acid, and mucic acid; they contain, therefore, the aldehyde-group. Levulose, on the other hand, is only very slowly acted on by cold bromine-water, and is destroyed by more powerful oxidising agents. All three sugars combine with hydrogen cyanide; on hydrolysis, the cyanhydrin obtained from dextrose and galactose yields normal heptylic acid, whilst that obtained from levulose gives methylbutylacetic acid. Both dextrose and galactose combine with phenylhydrazine and with hydroxylamine just like simple aldehydes.

The one argument which is still brought against the aldehyde formula, namely, that dextrose and galactose do not give the characteristic reaction of aldehydes with a sulphurous acid solution of rosaniline, cannot be regarded as of much importance, because no simple fatty hydroxy-aldehyde has yet been tested with this reagent.

The great want of a suitable method for the isolation of sugars was supplied by the discovery of the phenylhydrazine reaction (Abstr., 1885, 53). When a warm 10 per cent. aqueous solution of dextrose is warmed for 10—15 minutes with a solution of phenylhydrazine in dilute acetic acid, glucosazone, $C_{18}H_{22}N_4O_4$, is deposited in crystals. The formation of this substance takes place in two phases (Abstr., 1887, 567); the sugar first combines with the base (1 mol.) like an ordinary aldehyde, forming a readily soluble hydrazone, but in presence of excess of phenylhydrazine the hydrazone undergoes a peculiar oxidation, one $CH_2\cdot OH$-group being converted into the carbonyl-group, which then reacts with the base (1 mol.) in the usual way.

The fact that the osazone obtained from dextrose is identical with that formed from levulose proves, not only that this explanation of the reaction is correct, but also that both compounds have the constitution $CH_2(OH)\cdot[CH(OH)]_3\cdot C(N_2HPh)\cdot CH{:}N_2HPh$.

All natural sugars which reduce Fehling's solution, including lactose and maltose, behave in this way with phenylhydrazine, as do also all aldehydes and ketones which contain a $CH_2\cdot OH$- or $CH\cdot OH$-

group adjacent to the aldehyde- or carbonyl-radicle. The hydrazones of most of the naturally occurring sugars are readily soluble in water, but mannose and its optical isomerides, and the various artificial sugars containing 7, 8, and 9 carbon-atoms (comp. this vol., p. 1230), form hydrazones, which are only sparingly soluble, and which can therefore be most conveniently employed for the identification or isolation of these sugars, into which they can be reconverted by decomposition with hydrochloric acid. When a hydrazone is vigorously shaken with hydrochloric acid of sp. gr. 1·19 at the ordinary temperature, a brown solution of the hydrochloride is obtained, but after one to two minutes the separation of phenylhydrazine hydrochloride commences, and in 10 to 15 minutes decomposition is complete; the sugar can be easily isolated from the filtered solution.

Of far more value for the identification of sugars are the almost insoluble, crystalline osazones, which differ from one another in solubility, melting point, and optical behaviour. On reduction with zinc-dust and glacial acetic acid, they are converted into basic compounds. Glucosazone, for example, yields the compound

$$CH_2(OH)\cdot[CH(OH)]_3\cdot CO\cdot CH_2\cdot NH_2,$$

one hydrazine-group being displaced by oxygen, the other being converted into an amido-group, with elimination of aniline; when this base is treated with nitrous acid in the cold, it is converted into levulose (Abstr., 1888, 39). As the other bases obtained in like manner do not crystallise well, the reconversion of the osazones into the sugars is best effected by decomposing them with fuming hydrochloric acid (Abstr., 1888, 1267). When finely divided glucosazone is quickly heated to 40° with fuming hydrochloric acid, the solution kept at this temperature for one minute, and then cooled to 25°, phenylhydrazine hydrochloride separates in crystals, and in 10 minutes the reaction is at an end; the filtered solution contains glucosone, which can be isolated in the form of its insoluble lead compound.

Glucosone has not yet been obtained in crystals; its reactions show that it is the aldehyde of levulose, $CH_2(OH)\cdot[CH(OH)]_3\cdot CO\cdot COH$, and its formation is expressed by the equation—

$$C_6H_{10}O_4(N_2HPh)_2 + 2H_2O = C_6H_{10}O_6 + 2N_2H_3Ph.$$

It combines with phenylhydrazine, yielding glucosazone; it gives crystalline quinoxaline-derivatives with aromatic orthodiamines, and on reduction with zinc-dust and acetic acid, it is completely converted into levulose.

It seems probable that other, as yet unknown, ketone-sugars can be obtained from the aldehyde-sugars by the same method as that employed in the transformation of dextrose into levulose. The inverse process, namely, the conversion of a ketone- into an aldehyde-sugar, has already been carried out as follows:—Levulose can be reduced to mannitol, which, on oxidation with nitric acid, gives the aldehyde mannose, and from the latter dextrose can be obtained in the manner described below.

The osazones may also be employed for ascertaining the molecular

formula of a sugar, as was done in the case of arabinose, sorbinose, and xylose; also for determining its constitution, as exemplified by the case of rhamnose and lactose.

The hydrazones and osazones are also particularly valuable for the detection of new sugars and sugar-like substances, witness the case of mannose, the true aldehyde of mannitol, a sugar which, first prepared artificially by the oxidation of the alcohol, was soon afterwards detected in the vegetable kingdom by Tollens and Gans, and by R. Reiss (Abstr., 1889, 687), who named it seminose. Erythrose and glycerose, two sugar-like substances, obtained by the oxidation of erythrol and glycerol respectively (Abstr., 1888, 1264), were also isolated by means of their osazones.

Glycerose, which is most conveniently obtained by the oxidation of glycerol with bromine and sodium carbonate, was proved to have the molecular formula $C_3H_6O_3$ by the analysis of the osazone, but it is probably a mixture of glyceraldehyde and dihydroxyacetone; when treated with dilute alkalis, it gives α-acrose (Abstr., 1888, 358), for the formation of which glyceraldehyde is necessary, and it combines with hydrogen cyanide, yielding a cyanhydrin, which on hydrolysis is converted into trihydroxyisobutyric acid (Abstr., 1889, 478), a compound that can only be formed from dihydroxyacetone.

The first step in the synthesis of sugars was made by Butlerow (*Annalen*, **120**, 295), the discoverer of methylenitan, a yellowish, sweet syrup, obtained by treating a hot solution of trioxymethylene with calcium hydroxide; this substance shows the usual reactions of sugars, but is optically inactive, and seems not to ferment with yeast. The method of preparing formaldehyde having been greatly improved by Loew (Abstr., 1886, 609), it became possible to examine the condensation of this substance more fully, which soon led to the discovery of formose (*ibid.*, 610). This compound, which was obtained by Loew by the condensation of formaldehyde with calcium hydroxide, was thought by him to be different from methylenitan, and to have the composition $C_6H_{12}O_6$; the author proved, however (Abstr., 1888, 590), that both substances consist of various sugar-like compounds, and are practically identical, the principal constituent of both being a sugar (formose) of the composition $C_6H_{12}O_6$, another sugar, α-acrose, being also present in the two mixtures. A little later Loew (Abstr., 1889, 581) obtained a sugar, which he named methose, by the condensation of formaldehyde by the action of lead and magnesium oxides, but this product was proved by the author to be identical with α-acrose. In the meantime (Abstr., 1887, 651, and 1888, 39), it was found that two isomeric sugars, α- and β-acrose, are formed when acraldehyde bromide is treated with a cold solution of barium hydroxide; these two substances, which can be most conveniently prepared by treating glycerose with cold dilute alkalis, can be isolated from various other sugar-like substances, which are produced at the same time, by means of their osazones, the latter being reconverted into the sugars by treatment with hydrochloric acid, in the manner described above.

α-Acrose, which is only obtained in small quantities, seems to be formed by a sort of aldol condensation of equal molecules of

glyceraldehyde and dihydroxyacetone, in accordance with the equation—

$$CH_2(OH)\cdot CH(OH)\cdot CHO + CH_2(OH)\cdot CO\cdot CH_2\cdot OH = CH_2(OH)\cdot[CH(OH)]_3\cdot CO\cdot CH_2\cdot OH;$$

its formation from glycerose and from formaldehyde takes place under conditions which exist in the vegetable kingdom, and is, therefore, of far greater interest than its preparation from acraldehyde bromide.

The remarkable resemblance of α-acrosazone to glucosazone, from which it differs principally in being optically inactive, at once led the author to suppose that α-acrose was the optically inactive form of dextrose or levulose. On decomposition with hydrochloric acid, α-acrosazone yields a sweet syrup which ferments with yeast, gives levulinic acid with hydrochloric acid, and, on reduction with sodium amalgam, is converted into a crystalline hexahydric alcohol, α-acritol (Abstr., 1889, 484), the resemblance of which to mannitol is so close that it was thought to be simply the inactive form of this naturally occurring alcohol. But for the fortunate discovery that α-acritol can be prepared from mannose, it would have been a task of considerable difficulty to prove its relationship to mannitol, as only 0·2 gram of α-acritol is obtained from 1 kilo. of glycerol.

When mannose, the aldehyde of mannitol, is oxidised with bromine-water, it is converted into a monocarboxylic acid, mannonic acid, $C_6H_{12}O_7$, which can be purified by means of the hydrazide by the method previously described (this vol., p. 152). On evaporating an aqueous solution of the acid, a crystalline lactone, which differs from the lactone of arabinosecarboxylic acid only in possessing an opposite rotatory power, is obtained; when these two lactones are mixed together in aqueous solution, they combine to form an optically inactive lactone. On reduction with sodium amalgam in the manner already described (this vol., p. 1149), the three lactones are converted into a dextro-rotatory, levo-rotatory, and inactive mannose respectively; these sugars, on further reduction, yield the corresponding active and inactive mannitols, the inactive modification being identical with synthetical α-acritol.

The relationship between all the known members of the mannitol series is shown in the table on the following page, the letters *d*, *l*, and *i* (from dexter, lævus, and inactive) serving to distinguish the various isomerides; the compounds marked with an asterisk are new, and will be described in a future paper.

Now since i-mannitol is identical with the α-acritol obtained synthetically, and α-acrose, obtained from α-acrosazone, is identical with i-fructose (this vol., p. 466), all that remains to complete the synthesis of a natural sugar is to convert a member of the inactive into a member of the active series. This can be accomplished in the case of the sugars themselves, through the agency of yeast. When an aqueous solution of synthetical α-acrose (i-fructose) is fermented with yeast, the solution, which was previously inactive, becomes strongly dextro-rotatory, and yields a glucosazone which is dextro-rotatory; this solution contains a sugar which is named

Mannitol Series.

l-Fructose.	i-Fructose. (α-Acrose).	d-Fructose. (Fruit-sugar).
	i-Glucosone.	d-Glucosone.

Mannose Group.

l-Mannonic acid. (Arabinosecarboxylic acid).	i-Mannonic acid.	d-Mannonic acid.
l-Mannose.	i-Mannose.	d-Mannose.
l-Mannitol.	i-Mannitol. (α-Acritol).	d-Mannitol.
l-Mannosaccharic acid. (Metasaccharic acid).	*i-Mannosaccharic acid.	*d-Mannosaccharic acid.

Glucose Group.

*l-Gluconic acid.	*i-Gluconic acid.	d-Gluconic acid.
*l-Glucose.	*i-Glucose.	d-Glucose. (Grape-sugar).

Alcohols wanting.

*l-Saccharic acid.	*i-Saccharic acid.	d-Saccharic acid.

l-frnctose, in spite of the fact that it is dextro-rotatory, because the letters *d* and *l* do not denote in every case the irregularly changing rotatory power, but express rather the chemical relationship between the compounds ; the letter *d* was chosen for the group of natural sugars, because most of them are dextro-rotatory, and although levulose is levo-rotatory, it belongs to the same geometrical series as d-mannose.

i-Mannose ferments with yeast just like i-fructose, the dextro-rotatory modification being destroyed, and the levo-rotatory modification remaining unchanged (this vol., p. 446), so that in both cases the yeast uses that part of the sugar to which it has been accustomed in the past.

As fermentation gives the less interesting compounds of the *l*-series only, chemical methods have to be employed for obtaining the natural sugars. i-Mannitol, on careful oxidation with nitric acid, yields i-mannose, which is converted into i-mannonic acid by treatment with bromine-water; by means of its strychnine or morphine salt, this acid can be separated into d- and l-mannonic acids, which, on reduction, give the optically active mannoses and mannitols. The d-mannose obtained in this way can be transformed into d-fructose (levulose) by means of its glucosazone, which is identical with that of dextrose and of levulose. The conversion of dextrose into mannose, and *vice versâ*, can be

accomplished by means of the acids. When gluconic acid is heated with quinine at 140°, it is partially converted into d-mannonic acid; the latter, under the same conditions, gives considerable quantities of d-gluconic acid, which on reduction yields d-glucose (dextrose), the synthesis of this natural sugar being thus completed.

l-Mannonic acid, in like manner, can be converted into the optical isomeride, l-gluconic acid, but the process is difficult to carry out, and the yield is small.

l-Gluconic acid can be more conveniently obtained, together with arabinosecarboxylic acid (l-mannonic acid), by treating arabinose with hydrocyanic acid and hydrolysing the product; this is the first instance of the formation of two stereochemical isomerides by the combination of an aldehyde with hydrogen cyanide.

The two active gluconic acids are very similar in appearance, and combine in aqueous solution yielding an inactive acid which forms salts and other inactive derivatives; on reduction, they are converted into the corresponding optically active isomerides of dextrose, namely, l- and i-glucose, and on oxidation they yield l- and i-saccharic acid.

The isomerism of all the compounds included in the above table can be explained in accordance with Le Bel and Van't Hoff's hypothesis, but the views at present held on the combination of isomeric compounds containing asymmetrical carbon-atoms will probably have to be modified.

Since all the members of the mannitol series can be prepared from their elements, the most important natural sugars have now been synthesised; but it is possible to prepare artificially sugars containing 7, 8, 9, &c., carbon-atoms by converting one containing 6 carbon-atoms into the acid containing 7, by means of hydrogen cyanide, and then reducing the lactone of this acid with sodium amalgam. The sugar containing 7 carbon-atoms produced in this way can then be employed for continuing the process up the series; mannoheptose,* mannooctose, and mannononose have already been prepared (compare this vol., p. 1230).

Many of these new synthetical sugars will certainly be found in the vegetable kingdom, and, even already, it has been proved that the heptahydric alcohol, formed by the reduction of mannoheptose, is identical with perseitol, $C_7H_{16}O_7$, a compound which occurs in the fruit of *Laurus persea*.

The most interesting result of these investigations is, however, the synthesis of dextrose and levulose, which throws some light on one of the most important and most wonderful physiological processes, namely, the formation of carbohydrates in green plants. As far as is known, these two sugars are not only the first products of assimilation, but they are also the material from which all other organic constituents of plants are prepared. Since it has not yet been proved that formaldehyde occurs in plants in any appreciable quantity, it seems probable that a search for other intermediate products, such as glycerose, might be attended with success. The fact that the active

* The system of nomenclature suggested for the sugars has been already explained (this vol. p. 598).

sugars only are formed in plants, whilst inactive acrose is alone produced by chemical synthesis, is still more interesting, as the question arises whether the formation of optically-active substances is a prerogative of plants—the result it may be of a kind of vital force? The answer to this question is probably in the negative, and it is, doubtless, but incomplete knowledge that gives an appearance of the wonderful to the process. No facts are known which directly negative the view that plants first prepare inactive sugars, and then split them up, making use of the members of the d-mannitol series for the production of starch, cellulose, inulin, &c., the optical isomerides serving to fulfil other functions.

Another interesting problem is, what would be the effect if some of the artificial sugars were supplied to animals, instead of the natural products? Mannose, which is so nearly related to dextrose, would probably serve as nutriment, even to the more highly organised animals, and the slight change in food might produce corresponding changes in assimilation. The liver, for example, might secrete a new glycogen, the mammæ a substitute for lactose. The consequence of substituting a pentose or a heptose, or, more especially, the fermentable nonose, for ordinary sugar might be far more important, and it would not be surprising if, under such circumstances, the functions of the blood and the tissues were modified; the pig, for example, secreting a different fat, the bee a different wax. As, moreover, with the help of fungi, plants prepare not only the more complex carbohydrates and fats, but albuminoïds as well, they might be forced to form different albuminoïds if supplied with some new sugar; a change of architecture, under chemical influence, might in this way be brought about, which would lead to the most remarkable results, and produce changes of form more fundamental than it has yet been found possible to do by crossing and selection. Although in the past hundreds of organic substances have been supplied to animals in order to determine what changes they undergo in the system, the materials used had invariably no resemblance whatever to natural food-stuffs; in the possession of new sugars, the physiologist will have a fruitful field of research, his labours in which are likely to lead to remarkable results.

For the chemist there remains work enough, even in the group of the carbohydrates; in accordance with present theories sixteen hexoses, of the same structure as dextrose, without counting the inactive forms, can exist in the dulcitol series, and, probably, all these compounds are actually capable of existence. It may even be said, with some assurance, that their preparation by the methods employed in the mannitol series will not be exceptionally difficult, as soon as it has been found possible to convert the various tartaric acids into the optically isomeric trihydroxybutyric acids.

The synthesis of starch, cellulose, inulin, gum, &c., is only a question of time, and, judging from the great strides which have been made in organic synthesis during the last 62 years, the chemist need have no hesitation in attempting to prepare synthetically any product whatever of the living organism. F. S. K.

Sugars Richer in Carbon, from d-Mannose. By E. FISCHER and F. PASSMORE (*Ber.*, **23**, 2226—2239).—d-Mannose, which can be prepared in large quantities from vegetable ivory-nuts (compare Fischer and Hirschberger, this vol., p. 224), can be more readily converted into the carboxylic acid by means of hydrocyanic acid than the other natural sugars. It has, therefore, been employed for the synthesis of some higher sugars in the manner described below; as the compounds produced all crystallise well, the authors have experienced no difficulties in continuing the process up to the formation of the compound $C_9H_{18}O_9$. The sugars obtained in this way are named d-mannoheptose, d-mannooctose, and d-mannononose, in accordance with the system of nomenclature already proposed (this vol., p. 598), the corresponding acids being termed d-manno-heptonic, -octonic, and -nononic acids respectively, and the alcohols, heptitol and octitol. All these compounds contain a normal chain of carbon-atoms, and the three synthetical sugars are all aldehydes.

d-Mannoheptonic acid, $C_7H_{14}O_8$ (previously called mannosecarboxylic acid, compare Abstr., 1889, 482), is prepared by heating ivory-nut shavings with hydrochloric acid as already described (this vol., p. 224), neutralising the filtered solution with lead carbonate, precipitating the lead with sodium carbonate, and evaporating the solution of mannose (2 kilos.), obtained in this way, to a syrup. The syrup is dissolved in water (4 parts), treated, in eight separate portions, with the theoretical quantity of hydrocyanic acid and a few drops of ammonia, the mixture kept for three days at the ordinary temperature, then heated at 50° for four hours, and barium d-mannoheptonate prepared from it in the manner already described (Abstr., 1889, 482); the weight of the pure salt thus obtained is about the same as that of the sugar employed. The barium salt is then dissolved in hot water (10 parts), the base exactly precipitated with sulphuric acid, the filtrate decolorised with animal charcoal, and evaporated; the crystalline residue consists of a mixture of mannoheptonic acid and its lactone, from which the acid can be isolated in a pure condition by recrystallising several times from hot water.

d-Mannoheptonic acid melts at 175°, being converted into the lactone, the same change occurring when it is heated at 130°, and also (but only partially) when it is kept over sulphuric acid, or boiled with water or alcohol. It is soluble in 25 parts of water at 30°, the solution being feebly levo-rotatory. The *sodium* salt, $C_7H_{13}O_8Na$, crystallises in long needles, melts at 220—225°, and is rather sparingly soluble in cold water. The lactone (Abstr., 1889, 482) has a sweet taste, and its specific rotatory power is $[\alpha]_{D20} = -74.23$.

d-Mannoheptose, $C_7H_{14}O_7$, is obtained as follows:—The pure lactone (10 grams) is dissolved in water (100 c.c.), mixed with 20 per cent. sulphuric acid (1 c.c.), the solution cooled to its freezing point, and $2\frac{1}{2}$ per cent. sodium amalgam (120 grams) added in the course of 30 to 40 minutes, the whole being vigorously shaken and kept acid by the frequent addition of dilute sulphuric acid; the decanted solution is now mixed with soda in such quantity that it remains slightly alkaline after keeping for 15 minutes, so as to convert any unchanged lactone into the sodium salt of the acid; the filtered solution

is then exactly neutralised with sulphuric acid in the cold, evaporated at 100° until crystallisation commences, and poured into boiling absolute alcohol (10 parts). The precipitated sodium salts are redissolved in hot water, again precipitated with alcohol, and the alcoholic mother liquors from the two operations evaporated, when the sugar remains as a syrup which crystallises after one to two days' time; the yield is, on the average, 40 per cent. of the lactone employed.

The compound prepared in this way still contains a little inorganic matter and small quantities of the heptahydric alcohol, but it can be directly employed for the synthesis of the higher sugars. About half the lactone is converted into mannoheptonic acid in the reduction process, and is recovered in the form of the sodium salt, mixed, however, with sodium sulphate; this mixture is dissolved in the least possible quantity of hot water, the solution cooled, and excess of dilute sulphuric acid added before crystallisation commences; after remaining for a long time most of the heptonic acid is deposited in crystals.

The crude mannoheptose, prepared in the manner described, can be freed from ash by recrystallisation from 96 per cent. alcohol, but it still contains heptitol (see below), from which it cannot be separated, except by converting it into the hydrazone. This compound is gradually precipitated in crystals when phenylhydrazine acetate is added to a cold aqueous solution of the crude sugar, and can be obtained in a pure state by recrystallisation from hot water. It is dissolved in fuming hydrochloric acid (4 parts), the solution kept for 15 minutes at 20°, then cooled well, filtered, the filtrate diluted, neutralised with lead carbonate, the filtered solution rendered alkaline with barium hydroxide, and shaken with ether until free from phenylhydrazine. The residual solution is then treated with a slight excess of sulphuric acid, freed from hydrochloric acid and sulphuric acid in the usual manner, shaken with animal charcoal until colourless, evaporated under reduced pressure, and the residual syrup, which soon solidifies when covered with alcohol, recrystallised from this solvent; the yield of pure sugar is 39 per cent. of the hydrazone employed.

d-Mannoheptose crystallises in slender needles, melts at 134—135° (corr.) to a coloured liquid, turns brown at about 190°, has a sweet taste, and is very readily soluble in water, but only very sparingly in boiling alcohol; it seems to crystallise from dilute methyl alcohol with 1 mol. H_2O. Its specific rotatory power, 10 minutes after solution, is $[\alpha]_{D20} = 85{\cdot}05$, but it gradually decreases, and, after 24 hours, has become constant, being then $[\alpha]_{D20} = 68{\cdot}64$. It gives all the usual reactions of sugars, and, like d-mannose, it is precipitated from its aqueous solution by basic lead acetate. When yeast is placed in a 10 per cent. aqueous solution of the sugar, kept at 30°, no fermentation takes place in the course of 24 hours.

The *hydrazone*, $C_7H_{14}O_6{:}N_2HPh$, crystallises from hot water in slender, colourless needles, melts at 197—200° with decomposition when quickly heated, and is only very sparingly soluble in cold water. Its freshly-prepared solution in fuming hydrochloric acid, diluted with water, is optically inactive, but in 45 minutes it shows a dextro-

rotation of 0·45°; in this respect it differs from the sparingly soluble hydrazones of d- and l-mannose.

d-Mannoheptosazone, $C_7H_{12}O_5(N_2HPh)_2$, separates in slender needles, when an aqueous solution of the hydrazone is heated with phenylhydrazine acetate. It crystallises from hot alcohol in slender needles, melts with decomposition at about 200°, when quickly heated, and is very sparingly soluble in hot alcohol, and almost insoluble in water and ether; its solution in glacial acetic acid is dextro-rotatory.

Heptitol (perseitol), $C_7H_{16}O_7$, is obtained when mannoheptose is reduced with sodium amalgam as described in the preparation of mannose (this vol., p. 466); the yield is about 70 per cent. of the sugar employed. A direct comparison of this synthetical alcohol with perseitol, which has been shown by Maquenne (Abstr., 1889, 32) to be a heptahydric alcohol, proved the identity of the two compounds, as does also the fact that Maquenne's perseitol, on oxidation with nitric acid of sp. gr. 1·14, is converted into mannoheptose.

d-Mannoctonic acid can be prepared from crude crystalline mannoheptose by treating it with hydrocyanic acid and a few drops of ammonia, as described in the preparation of the heptonic acid; as the barium salt does not crystallise well, the acid is best purified by heating its dilute aqueous solution with phenylhydrazine and acetic acid. The *hydrazide*, $C_8H_{15}O_8 \cdot N_2H_2Ph$, which is gradually deposited from the solution, crystallises from hot water in colourless needles melting at about 243° with decomposition when quickly heated; it is almost insoluble in cold water and alcohol, and rather sparingly soluble in hot water. It is reconverted into the acid by boiling with barium hydroxide, as previously described (this vol., p. 153), but the acid was not isolated; the solution, freed from barium hydroxide and phenylhydrazine, and decolorised with animal charcoal, is evaporated, and the residual mannoctolactone, which gradually solidifies when treated with alcohol, purified by recrystallisation from this solvent. 30 grams of mannoheptose yield 19 grams of the pure lactone.

Mannoctolactone, $C_8H_{14}O_8$, melts at about 167—170° with decomposition, has a sweet taste, and is very readily soluble in water, the solution becoming slightly acid after some time; it dissolves rather freely in hot alcohol, and its specific rotatory power is $[\alpha]_{D20} = -43 \cdot 58$.

d-Mannoctose is obtained from the lactone (1 part) exactly as described in the case of mannoheptose, except that a larger quantity (16 parts) of $2\frac{1}{2}$ per cent. sodium amalgam is required; on evaporating its alcoholic solution, there remains a sweet syrup, which does not crystallise even when purified by means of the hydrazone. It is very readily soluble in water, only very sparingly in absolute alcohol, is levo-rotatory, and does not ferment with yeast. The *hydrazone*, $C_8H_{16}O_7{:}N_2HPh$, crystallises from hot water, in which it is sparingly soluble, in colourless needles, and melts, when quickly heated, at about 212° with decomposition. The *osazone*, $C_8H_{14}O_6(N_2HPh)_2$, is gradually deposited in yellow needles when a dilute aqueous solution of the sugar, or of the hydrazone, is warmed with excess of phenylhydrazine acetate; it is almost insoluble in hot water and boiling alcohol, and melts at about 223° with decomposition.

d-*Mannoctitol*, $C_8H_{18}O_8$, prepared from the sugar by reducing it with sodium amalgam as described under mannoheptose, separates from hot water, in which it is only moderately easily soluble, in colourless, microscopic plates, sinters together at 250°, and melts completely at 258°; when heated in small quantities, it volatilises without leaving any carbonaceous residue.

d-*Mannononic lactone*, $C_9H_{16}O_9$, can be obtained by treating mannoctose with hydrocyanic acid, converting the product into the hydrazide of mannononic acid, and decomposing the latter with barium hydroxide exactly as described in the case of the lower homologue; on evaporating the aqueous solution of the acid to a syrup, it is almost completely converted into the lactone, which, when treated with alcohol, gradually solidifies. It crystallises from hot alcohol in slender needles, melts at 175—177°, and is readily soluble in water, and moderately easily in hot alcohol; it has a sweet taste, and its specific rotatory power is $[\alpha]_{D20} = -41°$.

d-*Mannononose*, $C_9H_{18}O_9$, can be obtained from the lactone without difficulty by the same method as that employed in the preparation of mannoctose; it separates from hot alcohol in small nodules, but it has not yet been obtained free from ash, sufficient material not having been prepared to allow of its purification by means of the hydrazone. It melts at about 130°, and is dextro-rotatory. The *hydrazone*, $C_9H_{18}O_8{:}N_2HPh$, crystallises from hot water in colourless needles, melts at about 223° with decomposition when quickly heated, and is very sparingly soluble in cold water. The *osazone* crystallises in yellow needles, melts at about 217° with decomposition, and is almost insoluble in hot water and alcohol.

Mannononose ferments with yeast just as readily as mannose and grape-sugar, carbonic anhydride being evolved, and a solution obtained which has an odour of alcohol, and which gives the iodoform reaction very distinctly. It is a curious fact that most of the sugars, such as glycerose, the hexoses, and mannononose, which contain three, or a simple multiple of three, carbon-atoms ferment with yeast, whereas the pentoses (arabinose and xylose), mannoheptose, and mannoctose do not.

Mannononose resembles dextrose so closely that the two compounds can be easily mistaken for one another; they have, moreover, the same percentage composition, approximately the same rotatory power, almost the same melting point, and both ferment with yeast, so that if mannononose had been obtained from the vegetable kingdom before the hydrazone test was known, it would certainly have been mistaken for dextrose. The occurrence of mannononose in plants would not be surprising, because it is more than probable that glyceraldehyde is formed in the vegetable kingdom; this compound so easily condenses to hexoses that it seems likely that, under other conditions, it might undergo condensation to mannononose.

The optical behaviour of the compounds described above is worthy of note, the rotatory power changing in an irregular manner from right to left and *vice versâ*, as is shown by the following table:—

d-Mannose Series.

Hexonic lactone..	+53·81°	Octonic lactone..	−43·58°
Hexose	+12·96	Octose	−3·3 (approx.).
Heptonic lactone.	−74·23	Nononic lactone .	−41·0
Heptose	+85·05	Nonose	+50·0 (approx.).

F. S. K.

The Sulphines and the Different Valencies of Sulphur. By R. NASINI and A. SCALA (*Gazzetta*, **19**, 526—528).—This is a paper of a polemical character containing a reply to Klinger and Maassen (Abstr., 1888, 357; 1889, 1135). The authors maintain that the measurements given by them and La Valle (Abstr., 1889, 115) fully establish the isomerism of the platinochlorides of diethylmethylsulphine and ethylmethylethylsulphine, the former crystallising in the cubic, and the latter in the monoclinic system as stated by Krüger (Abstr., 1877, 186). S. B. A. A.

Myristic Aldehyde. By F. KRAFFT (*Ber.*, **20**, 2360—2364; compare Abstr., 1889, 1017).—Tetradecyl alcohol, $C_{13}H_{27}·CH_2·OH$, is obtained by reducing myristic aldehyde with sodium in alcoholic solution. The *hydrogen sodium sulphite* compound, $C_{14}H_{29}O·SO_3Na$, is prepared by heating myristic aldehyde with a saturated aqueous solution of hydrogen sodium sulphite at 55°; it crystallises from alcohol in colourless plates, and slowly decomposes at 130° without melting. The corresponding *potassium* compound is very similar in properties. *Tetradecylaldoxime*, $C_{13}H_{27}·CH:NOH$, is obtained by treating the aldehyde with half its weight of hydroxylamine hydrochloride in alcoholic solution; it crystallises from alcohol in silvery, lustrous plates melting at 82°, and has a slight peppermint-like odour. *Tetradecylamine*, $C_{14}H_{24}·NH_2$, is formed by the reduction of the aldoxime with sodium amalgam in alcoholic solution, to which acetic acid is added from time to time; it melts at 37°, boils at 162° under a pressure of 15 mm., and is most readily purified by distillation; it rapidly absorbs carbonic anhydride on exposure to air. The same compound may also be obtained by reducing myristonitrile, $C_{14}H_{27}N$, with sodium in alcoholic solution. The *hydrochloride*, $C_{14}H_{29}·NH_2,HCl$, is readily soluble in water; it crystallises from ether in lustrous plates, which decompose on heating. The *platinochloride* has also been prepared. *2′-Tridecylquinoline*, $C_9H_6N·C_{13}H_{27}$, is formed by the distillation of the product obtained by the action of aniline and pyruvic acid on tetradecylaldehyde. It crystallises in large, white plates melting at 31—32°. The *hydrochloride* and *platinochloride* have been prepared; the latter crystallises in yellow, lustrous plates. *Dodecylamine*, $C_{12}H_{25}·NH_2$, is formed by the reduction of lauronitrile with sodium in alcoholic solution; it melts at 27—28°, and boils at 134—135° under a pressure of 15 mm. (compare Lutz, Abstr., 1886, 685). J. B. T.

Reduction-products of 1 : 2-Diketones. By H. v. PECHMANN and F. DAHL (*Ber.*, **23**, 2421—2427; compare Abstr., 1889, 1137).—Dimethylketol, COMe·CHMe·OH, is prepared by warming diacetyl

(20 grams) with granulated zinc (30 grams), and dilute (1 : 5) sulphuric acid (280 grams); the product is extracted 20 times with ether, the ether cautiously evaporated, and the residue dried over anhydrous sodium sulphate. The yield is quantitative; the ketol boils at 141—142°, has a sp. gr. of 1·0021 at 15°/4°, and is miscible with all the ordinary solvents except light petroleum. It reduces Fehling's solution, and is readily oxidised on exposure to air. The *phenylhydrazone*, $CHMe(OH)\cdot CMe\colon N_2HPh$, is obtained by treating a mixture of the ketol and phenylhydrazine, in molecular proportion, with sodium acetate in aqueous solution; it separates as an oil, which solidifies on cooling. It crystallises from benzene, on the addition of light petroleum, in stellate groups of long prisms melting at 83—84°. It is readily soluble in alcohol, ether, chloroform, benzene, and dilute acids, but not in alkalis; it quickly undergoes decomposition on keeping. With excess of phenylhydrazine in the cold, the ketol yields a mixture of diacetylphenylhydrazone and diacetylosazone; the latter is also formed on warming the ketol with excess of phenylhydrazine. Dimethylketol does not solidify in a freezing mixture, but if allowed to remain for several weeks, or months, it becomes converted into a solid crystalline modification melting at 127—128°; the addition of a crystal of this compound to the liquid ketol does not hasten its solidification. A second solid modification is obtained by adding some indifferent substance, such as a piece of granulated zinc, to the liquid ketol; in a few hours it crystallises in colourless, thin plates melting at 96—98°; after some time the crystals liquefy spontaneously at ordinary temperatures, and then gradually pass into the modification of high melting point. These two substances are quite distinct, they may be sublimed without change by cautiously heating; they dissolve slowly in ordinary solvents, becoming converted into the liquid ketol, which is also formed by distilling, or melting, either of them. Both are optically inactive, but it appears probable that they are physical, rather than chemical, isomerides.

Methylethylketol, $COMe\cdot CHEt\cdot OH$, is prepared from acetylpropionyl; it is a colourless, sweet-smelling liquid, closely resembling the dimethyl-derivative in properties; it boils at 152—153°, and at 77° under a pressure of 35 mm.; its sp. gr. is 0·9722 at 17·5°/4°. On treatment with phenylhydrazine, the *phenylhydrazone* is formed. With excess of phenylhydrazine in the cold, acetylpropionyl-α-phenylhydrazone, $COEt\cdot CMe\colon N_2HPh$, is obtained, thus showing the constitution of the ketol. δ-Methylethylethylene glycol, $CHMe(OH)\cdot CHEt\cdot OH$, is prepared by reducing methylethylketol with sodium amalgam; it is identical with the compound obtained by Wagner and Saytzeff from δ-methylethylethylene bromide (compare Abstr., 1876, 547).

J. B. T.

Isophorone. By W. F. Laycock (*Annalen*, **258**, 230—234; compare Abstr., 1889, 487).—The higher boiling (115—150°) fractions of the oil obtained by distilling sugar with lime contain a considerable quantity of a mixture of ketones, probably the compounds $C_5H_{10}O$ and $C_6H_{12}O$, which can be separated from the other constituents of the oil by shaking with sodium hydrogen sulphite. The residue

contains a new furfuraldehyde-derivative, the presence of which can be proved as follows:—The oil is treated with phenylhydrazine, kept for some hours, the excess of phenylhydrazine removed by washing with dilute acetic acid, and the residual solution distilled with steam; the oil that passes over is fractionated, and the portion boiling between 115 and 130° is heated at 170° with concentrated hydrochloric acid, whereby the furfuraldehyde-derivative is converted into a 1.4-diketone. This diketone has the composition $C_7H_{12}O_2$, and boils at 197—200°; it does not give the aldehyde reactions, and it yields a pyrroline-derivative when boiled with ammonium acetate. The *dioxime*, $C_7H_{14}N_2O_2$, melts at 129° and is readily soluble in hot, but only sparingly soluble in cold water. The constitution of the ketone is represented by one of the formulæ

$$COMe{\cdot}CHMe{\cdot}CH_2{\cdot}COMe \text{ or } COEt{\cdot}CH_2{\cdot}CH_2{\cdot}COMe.$$

The presence of isophorone in the other fractions of the oil could not be detected; the compound described under this name by Benedikt (*Annalen*, **162**, 306) is evidently a mixture of various substances. F. S. K.

Electrolysis of Fatty Acids. By N. Bunge (*J. Russ. Chem. Soc.*, **21**, 525—557).—Referring to the work done previously by Kolbe, Kolbe and Kaempf, Brazier and Gossleth, Wurtz, Schorlemmer and Kekulé, the author considers the reaction a very complicated one, which cannot be represented by a simple chemical equation. The author's own earlier experiments with oxalic, formic, and mellitic acids have convinced him that Kekulé's general formulæ:

$$C_nH_{2n}(COOM)_2 = M_2 + 2CO_2 + C_nH_{2n} \text{ and}$$
$$2C_nH_{2n+1}{\cdot}COOM = M_2 + 2CO_2 + (C_nH_{2n+1})_2$$

are not in accordance with facts, and that the complicated groups set free at the anode are not decomposed into their simpler constituents, but that they enter into reaction with water, re-forming the original acid and oxygen, and that the latter, on being liberated, oxidises the electrolyte, and thus forms the different products.

The original paper contains a detailed description of the author's apparatus, the preparation of *pure* substances, and a large set of tabularly arranged analytical data of the gaseous products. It is shown also, that the nature and relative quantity of the products obtained at the anode vary very considerably with varying concentration, intensity of the current, size and surface of electrodes, and especially with the temperature of the electrolyte.

Potassium propionate yielded, besides carbonic anhydride and hydrogen, a large proportion of ethylene, and only a small quantity of butane, although the latter ought to be the chief product, if Kekulé's view were correct. As regards oxygen, this gas was not observed at 0°, but at 100° the quantity was much larger than that of the hydrocarbons. No definite relation could be traced between the quantities of ethylene and butane. *Free propionic acid* yielded very nearly the same product as its potassium salt. *Isobutyric acid*, when submitted to electrolysis at 0°, gave not the expected hexane, but only carbonic anhydride, propylene, hydrogen, and oxygen, and at 100° scarcely any

hydrocarbon. *Normal butyric acid* yielded propylene as the chief product, together with some butane, and a trace of a liquid hydrocarbon, probably hexane.

In order to test the correctness of Kolbe's and Kaempf's statement that acetic acid yields ethylene on electrolysis, the author prepared *pure* sodium acetate with the greatest care, and passed the products of electrolysis for 48 hours through bromine, but not a trace of ethylene bromide could be found. In all cases, the acids yielded small quantities of ethereal salts. The author remarks that india-rubber corks and joints are to be avoided in this kind of work, as a considerable absorption of hydrocarbons takes place, the india-rubber swelling up. In conclusion, the author says that the above view on the complexity of the chemical process in electrolysis, as first pronounced by Bourgoni, is entirely confirmed. B. B.

Oxidation of Cerotic Acid by Nitric Acid. By T. MARIE (*J. Pharm.* [5], **22**, 145—150).—When cerotic acid is oxidised with nitric acid of above 1·3 sp. gr., succinic acid is the chief product; the reaction is very violent, and the intermediate products are destroyed. Nitric acid of 1·15 sp. gr. gives much better results. After 48 hours' boiling, the cooled mass consists of a liquid and a superposed solid; these were examined separately. As the yield of acid formed by oxidation is only small, the products of 18 operations were united and examined together. The liquid contains the volatile acids caproic, valeric, acetic, and butyric; and the non-volatile acids sebacic, succinic, suberic, pyrotartaric, and probably adipic. The insoluble portion well washed and treated on the sand-bath with very dilute baryta-water yields soluble and insoluble barium salts which have the composition of the caprate, caprylate, and œnanthylate. The insoluble barium salts contained the undecomposed cerotic acid, and a nitro-derivative of cerotic acid whose lead salt is insoluble in ether.

J. T.

Decamethylenedicarboxylic Acid. By H. NOERDLINGER (*Ber.*, **23**, 2356—2359).—*Methyl undecylenate*, $C_{10}H_{19}\cdot COOMe$ is a colourless liquid, insoluble in water; it boils at 248° under a pressure of 760 mm., and at 124° at 10 mm. *Ethyl undecylenate*, $C_{10}H_{19}\cdot COOEt$ resembles the methyl compound, and boils at 259° under a pressure of 760 mm., and at 131·5° at 10 mm. *Methyl bromundecylenate*, $C_{10}H_{20}Br\cdot COOMe$, is prepared from methyl undecylenate by treatment with hydrobromic acid; it is a colourless, strongly refractive liquid, boiling at 165·5° under a pressure of 10 mm. *Ethyl bromundecylenate*, $C_{10}H_{20}Br\cdot COOEt$, is obtained in a similar manner to the methyl-derivative; it boils at 171—172° under a pressure of 10 mm. In order to prepare *decamethylenedicarboxylic* acid, $C_{10}H_{20}(COOH)_2$, either of the above brominated compounds is treated with potassium cyanide, and the product hydrolysed with alcoholic potash; on adding hydrochloric acid, a precipitate is formed consisting of a mixture of several acids; this is distilled, and the portion boiling above 230° under a pressure of 10 mm. is dissolved in ammonia. On adding barium chloride, the barium salt separates, and, from this, the pure acid may be obtained. It crystallises from water in slender, flat, lustrous needles, melting at

124·5—125·5°, and boiling at 245° under a pressure of 10 mm.; it is soluble in 891 parts of water at 100°, and in 22,225 parts at 23°. In its chemical and physical properties the acid is completely analogous to the lower homologues of the oxalic acid series. The *potassium*, *sodium*, and *ammonium* salts are soluble in water. All the remaining salts are sparingly soluble in cold water, and are deposited on warming the solution. The *silver* salt is obtained as a white powder, which becomes violet on exposure to light. J. B. T.

Haloïd Derivatives of Ethyl Acetoacetate. By A. HANTZSCH (*Ber.*, **23**, 2339—2342).—On treating ethyl acetoacetate with bromine, ordinary ethyl bromacetoacetate is formed, from which *ethyl amidothiazylacetate*, $NH_2{\cdot}C{\Large<}{\begin{matrix}S{\cdot}CH\\ \Vert\\ N{\cdot}C{\cdot}CH_2{\cdot}COOEt\end{matrix}}$, and *ethyl methylthiazylacetate*, $MeC{\Large<}{\begin{matrix}S{\cdot}CH\\ \Vert\\ N{\cdot}C{\cdot}CH_2{\cdot}COOEt\end{matrix}}$, are prepared by the action of thiocarbamide and thioacetamide respectively. These compounds are isomeric with the corresponding thiazole-derivatives obtained from ethyl chloracetoacetate which are represented by the formulæ, $NH_2{\cdot}C{\Large<}{\begin{matrix}S{\cdot}C{\cdot}COOEt\\ \Vert\\ N{\cdot}CMe\end{matrix}}$ and $MeC{\Large<}{\begin{matrix}S{\cdot}C{\cdot}COOEt\\ \Vert\\ N{\cdot}CMe\end{matrix}}$. Ethyl bromacetoacetate, prepared by the action of bromine on ethyl cupracetoacetate (compare Schönbrodt, this vol., p. 27), yields compounds identical with those obtained from the chloracetoacetate. It appears, therefore, that by the direct action of bromine on ethyl acetoacetate, the γ-derivative, $CH_2Br{\cdot}CO{\cdot}CH_2{\cdot}COOEt$, is formed, and that Schönbrodt's compound is really the α-derivative, $CHBrAc{\cdot}COOEt$, corresponding with the well-known chlorinated derivative. Ethyl methacetoacetate yields a γ-bromo-substitution product which combines with thiacetamide, and, after elimination of the carboxyl-group, forms *methylethylthiazole*, $MeC{\Large<}{\begin{matrix}S{\cdot}CH\\ \Vert\\ N{\cdot}CEt\end{matrix}}$. Chlorine, however, gives the α-derivative, from which *trimethylthiazole*, $MeC{\Large<}{\begin{matrix}S{\cdot}CMe\\ \Vert\\ N{\cdot}CMe\end{matrix}}$, is obtained by the action of thiacetamide. J. B. T.

Action of Alcoholic Potash on Bromisosuccinic Acid. By S. TANATAR (*J. Russ. Chem. Soc.*, **21**, 558—563).—Isosuccinic acid, prepared from ethyl α-bromopropionate, is treated with bromine at 100° to convert it into the dibromopropionic acid melting at 118—119°. This is boiled for four to five hours with alcoholic potash, the alcohol removed by distillation, and the residue acidified with hydrochloric acid, after which the liquid is extracted with ether. On distilling off the ether, an oil is left, which after some time becomes converted into a crystalline mass consisting of a mixture of two or three acids. The cold aqueous solution of these is saturated with milk of lime, and after some time filtered from the excess of lime and from the sparingly soluble calcium salt of an acid having the formula $C_8H_{10}O_9$.

The filtrate on being acidified with a few drops of hydrochloric and acetic acids and boiled, deposits a copious precipitate consisting of a calcium salt of one of the acids. This is purified by dissolving it in cold water and heating the solution, when it is again deposited. Its composition is $C_6H_8CaO_5$. The zinc salt is also more soluble in cold than in hot water. The silver salt has the formula $C_6H_8Ag_2O_5$. The acid itself, *adipomalic acid*, $C_6H_{10}O_5$, when crystallised from water or ether is deposited in small, glistening needles, which melt at 111°. At 150—160°, the acid is decomposed into carbonic anhydride and an oily acid, $C_5H_{10}O_5$, which the author considers to be β-hydroxyvaleric acid.

B. B.

Ethyl Oximidosuccinates. By A. Piutti (*Chem. Centr.*, 1890, i, 938—939; from *Ann. Chim. Farm.*, **11**, 161).—Of the three possible monethyl oximidosuccinates, the α-salt has been already described (Abstr., 1885, 1122), and also by the author the γ-salt (Abstr., 1889, 383), but the β-salt, COOH·C(NOH)·CH_2·COOEt, is still unknown. The author finds that diethyl oximidosuccinate is identical with the oxime of ethyl oxalacetate, and that the α-ethyl oximidosuccinate is converted into the γ-salt by the action of sodium ethoxide.

J. W. L.

Diacetamide. By W. Hentschel (*Ber.*, **23**, 2394—2401).—Diacetamide is best prepared by boiling acetamide (600 grams) with acetic anhydride (1250 grams) for half an hour in a reflux apparatus. The addition of sodium acetate is needless. The product is distilled, and the portion boiling below 125° is fractionated under a pressure of 10 mm.; the greater part passes over at about 108—109°; it is dissolved in 10 parts of pure ether, and the acetamide precipitated with gaseous hydrogen chloride; on cooling the clear solution, diacetamide separates in slender, white needles. This may be purified either by repeated recrystallisation from ether, or by moistening with water, adding barium carbonate, and evaporating nearly to dryness on the water-bath; the residue is then completely dried in a vacuum, and extracted with ether; on evaporation, pure diacetamide separates; it melts at 77·5—78°, and boils at 222·5—223·5°, not at 210—215° as stated by Gautier; under a pressure of 10 mm., the boiling point is 108—108·5°. Diacetamide burns with a non-luminous flame. On heating at 250° for two hours in a sealed tube, acetonitrile, acetic acid, and acetamide, together with unchanged diacetamide, are obtained. The reactions which take place are somewhat complicated; acetonitrile and acetic acid are first formed, but at higher temperatures these recombine; part of the acetic acid, however, acts on the diacetamide yielding acetamide. An aqueous solution of diacetamide is neutral, but becomes acid on prolonged boiling; the decomposition proceeds uniformly; after two hours' heating at the boiling point of methyl alcohol, 7·3 per cent. of the diacetamide is decomposed, after 12 hours' heating 43 per cent.; the products are acetic acid and acetamide. With mineral acids the decomposition proceeds very much more rapidly, ammonium salts being also formed. Concentrated sulphuric acid readily acts on diacetamide with production of acetic acid; with nitrous acid it yields ammonium nitrate and acetic acid. Neither acetic an-

hydride nor ammonia gas reacts with diacetamide; potassium hydroxide hydrolyses it to acetic acid and acetamide; the same result is obtained with sodium ethoxide. *Sodium diacetamide*, $NNaAc_2$, may be prepared by warming sodium with an anhydrous ethereal solution of pure diacetamide for 10 to 12 hours; it forms a very hygroscopic, white powder. Methylacetamide is obtained by heating the sodium compound with methyl iodide in a sealed tube at 120°. Triacetamide is formed by heating sodium acetamide with acetic chloride or anhydride, diluted with ether or benzene; it is separated by distillation and appears to boil at 93—94° under a pressure of 14 mm.; it solidities on cooling, but is a liquid at ordinary temperatures, thus differing in a very marked manner from the compound (m. p. 77—78) which has hitherto been regarded as being triacetamide. J. B. T.

Condensation of Carbamide with Ethyl Acetoacetate. By R. BEHREND and P. ERNERT (*Annalen*, **258**, 360—362).—Ethyl sodioacetoacetate and carbamide combine together in alcoholic solution, yielding a colourless, crystalline compound of the composition $C_{13}H_{22}N_2O_7Na_2$. This substance melts at about 165°, and crystallises unchanged from hot alcohol, but is decomposed by water; when dry it is not acted on by carbonic anhydride, but the moist substance is rapidly decomposed. On passing carbonic anhydride into its alcoholic solution, it is decomposed into carbamide, ethyl acetoacetate, and sodium ethyl carbonate, and when boiled with methyl iodide in alcoholic solution, it yields carbamide and ethyl acetoacetate, together with sodium iodide. F. S. K.

Diazouracilcarboxylic Acid and its Derivatives. By R. BEHREND and P. ERNERT (*Annalen*, **258**, 347—359; compare Abstr., 1888, 809).—*Diazouracilcarboxylic acid*, $\begin{matrix}CO\cdot NH\cdot C\cdot COOH\\ | \qquad\quad \| \\ NH\cdot CO\cdot C\cdot N{:}NOH\end{matrix}$, is deposited in needles containing water of crystallisation when amidouracilcarboxylic acid is digested with sodium nitrite and water, and the ice-cold, filtered solution acidified with hydrochloric acid. It is readily soluble in alkalis, but only sparingly in water, to which it imparts an acid reaction; when an aqueous solution is heated at 40—50° carbonic anhydride is evolved, and the solution turns purple, but on boiling, nitrogen is given off, and a yellow, amorphous substance is deposited on cooling. It is unstable, and when kept for a long time at the ordinary temperature it is converted into diazouracil.

Hydrazineuracilcarboxylic acid, $C_5H_6N_4O_4$, is obtained when the preceding compound is reduced with hydrochloric acid and stannous chloride in ice-cold aqueous solution; hydroxylamine is not formed in the reaction. It separates from hot 8 per cent. hydrochloric acid in ill-defined crystals, gradually decomposes at 100°, turns brown at 120°, and is insoluble in cold but soluble in hot water, yielding a red solution; it reduces Fehling's solution in the cold, and its constitution is probably expressed by the formula $\begin{matrix}CO\cdot NH\cdot C\cdot COOH\\ | \qquad\quad \| \\ NH\cdot CO\cdot C\cdot NH\cdot NH_2\end{matrix}$.

A compound of the composition $C_6H_8N_4O_3$ ($= C_4H_2N_4O_2,C_2H_6O$)

is formed with evolution of carbonic anhydride when freshly-prepared diazouracilcarboxylic acid is boiled with alcohol; it crystallises from alcohol in yellow plates, loses 1 mol. of alcohol at 100°, and explodes when heated on platinum foil. It is almost insoluble in cold alcohol, ether, and hot water, and it is decomposed by boiling water, potash, and hydrochloric acid.

A salt of the composition $C_4H_3N_4O_3K$ is formed when the preceding compound is agitated with the theoretical quantity of cold 1 per cent. potash; it crystallises in needles, is only sparingly soluble in water, and is decomposed by alcohol and alkalis.

Diazouracil, $C_4H_4N_4O_3$, is obtained when the salt just described is suspended in ice-cold water, and decomposed with concentrated hydrochloric acid, also when the compound of the composition $C_6H_8N_4O_3$ is boiled with water. It separates from hot water in crystals, is decomposed by warm dilute acids with evolution of nitrogen, and explodes when heated on platinum foil.

Hydrazineuracil hydrochloride, $C_4H_6N_4O_2,HCl$, prepared by reducing the compound of the composition $C_6H_8N_4O_3$ with stannous chloride and hydrochloric acid in well-cooled aqueous solution, crystallises in colourless plates, and is decomposed by boiling water; it reduces Fehling's solution in the cold, and when treated with sodium carbonate or acetate it yields yellow or reddish compounds, which seem to be decomposition-products of the base. The constitution of the base may be expressed by the formula $\begin{array}{l}\text{CO·NH·CH} \\ \vert \qquad\qquad \Vert \\ \text{NH·CO·C·NH·NH}_2\end{array}$.

F. S. K.

Derivatives of Diethylthiocarbamide. By G. Noah (*Ber.*, **23**, 2195—2200).—*Methyldiethylthiocarbamide hydriodide*, $C_6H_{14}N_2S,HI$, prepared by treating diethylcarbamide with methyl iodide, is a crystalline compound, very readily soluble in all ordinary solvents. The free *base* is a yellow, disagreeably-smelling oil, with a strong alkaline reaction. The *picrate*, $C_6H_{14}N_2S,C_6H_3N_3O_7$, separates from water in crystals melting at 116°. The *platinochloride*, $(C_6H_{14}N_2S)_2,H_2PtCl_6$, crystallises in plates.

Diethylguanidine is obtained when methyldiethylcarbamide is heated at 100° with alcoholic ammonia. It is a yellow oil, soluble in alcohol and ether; the *picrate*, $C_5H_{13}N_3,C_6H_3N_3O_7$, crystallises from water in long needles melting at 141°.

Triethylthiocarbamide hydriodide is deliquescent, and soluble in alcohol and ether. The *picrate*, $C_7H_{16}N_2S,C_6H_3N_3O_7$, crystallises in rhombohedra, and melts at 72°. The *platinochloride*,

$$(C_7H_{16}N_2S)_2,H_2PtCl_6,$$

is crystalline.

The picrate of *diethylpropylthiocarbamide* crystallises in plates, and melts at 65—66°.

Compounds analogous to those described above are obtained by treating diethylthiocarbamide with amyl iodide, allyl iodide, and benzyl chloride; *diethylamylthiocarbamide* and *diethylallylthiocarbamide* are colourless oils; *diethylbenzylthiocarbamide hydrochloride*, $C_{12}H_{18}N_2S,HCl$, crystallises in needles, and melts at 73—75°.

Diethylethylenepseudothiocarbamide, $\begin{matrix} CH_2—S \\ | \\ CH_2·NEt \end{matrix}\!\!>C:NEt$, is formed when diethylthiocarbamide is boiled with ethylene bromide for five to six hours, and the product decomposed with soda. It is a yellowish oil, boils at 224° (748 mm.), is volatile with steam, and is readily soluble in alcohol and ether, but only sparingly in water; its constitution is proved by the fact that, on oxidation with chlorine in dilute hydrochloric acid solution and subsequent decomposition with strong hydrochloric acid, it yields ethylamine, carbonic anhydride and taurine.

The *salt* $NHEt·C(NEt)·S·CH_2·CH_2·S·C(NEt)·NHEt,2HBr$ is obtained when diethylthiocarbamide is treated with ethylene bromide at a temperature below 100°. It separates from alcoholic ether in colourless needles, melts at 184°, and is readily soluble in water and hot alcohol, but insoluble in benzene and light petroleum; when heated with potash, it yields ethylene mercaptan.

Diethyltrimethylenepseudothiocarbamide, $C_8H_{16}N_2S$, prepared by boiling diethylthiocarbamide with trimethylene bromide, forms a crystalline platinochloride, $(C_8H_{16}N_2S)_2,H_2PtCl_6$, which melts at 119° with decomposition; when the diethyl base is warmed with trimethylene bromide at a temperature below 100°, the compound $C_{13}H_{18}N_4S_2$ is formed. F. S. K.

The Furfuran-group. Supposed Isomerides of Pyromucic Acid and of Furfuraldehyde. By V. OLIVERI and A. PERATONER (*Gazzetta*, **19**, 633—639; compare Maquenne, this vol., p. 33).—The authors find that Limpricht's isopyromucic acid (Abstr., 1873, 621), when thoroughly purified by crystallisation from benzene or toluene, is identical with ordinary pyromucic acid, since it melts at 128—131°, and yields an ethyl salt melting at 34—35° and boiling at 191°, and an amide melting at 141—142°. The β-pyromucic aldehyde (fucusaldehyde) obtained by Stenhouse dissolves in solutions of sodium hydrogen sulphite, but a small quantity of an oily, non-aldehydic substance may be extracted from the solution with ether. On adding a dilute solution of soda to the hydrogen sulphite and extracting with ether, a substance is obtained having the composition $C_5H_4O_3$, which distils between 158—160°, and has all the physical properties of furfuraldehyde. The hydrazones of these substances both crystallise in greyish laminæ melting at 90—92°. Fucusaldehyde was further converted into Stenhouse's β-pyromucic acid, which, after recrystallisation from toluene and benzene, has the same melting point as ordinary pyromucic acid (128—129°), and yields an identical ethyl salt and an amide.

It thus appears that fucusaldehyde is identical with furfuraldehyde, and that Limpricht's iso-acid and Stenhouse's β-acid are identical with ordinary pyromucic acid. S. B. A. A.

Conversion of Pyrroline into Tetramethylenediamine. By G. CIAMICIAN (*Gazzetta*, **19**, 578—580).—Ciamician and Dennstedt (*ibid.*, **14**, 156) observed that pyrroline unites with hydroxylamine, forming a solid compound, $C_4H_8N_2O_2$, which melts at 173°, and which they re-

garded as the dioxime of succinaldehyde, NOH:CH·CH_2·CH_2·CH:NOH. By treating this compound with sodium and absolute alcohol, a base is formed which is shown to be identical with tetramethylenediamine (putrescine) by its boiling point, 158—159°, the melting point of the benzoyl-derivative, 178°, and by the agreement of the crystalline form of the platinochloride and picrate with the corresponding tetramethylenediamine-derivatives. The hydrochloride of the base may be converted into pyrrolidine, and the aurochloride of the product is identical with that described by Ciamician and Magnaghi, melting with decomposition at 205—206°. The formation of tetramethylenediamine from pyrrolinehydroxylamine indicates the presence in the latter compound of the chain N·C·C·C·C·N; it is further probable that one molecule of pyrroline reacts with 2 molecules of hydroxylamine, the compound $(CH:CH·NH·OH)_2$ being first formed with elimination of ammonia, and subsequently converted into the more stable form $(CH_2·CH:NOH)_2$. Pyrrolinehydroxylamine somewhat resembles the glyoximes; it dissolves in alkalis, reacts with acetic anhydride, and evolves nitrous oxide when heated with nitrous acid. With phenylhydrazine, a dihydrazone, $(CH_2·CH:N_2HPh)_2$, is formed, which melts at 124—125°. S. B. A. A.

Action of Ethyl Oxalate on Pyrryl Methyl Ketone. By A. Angeli (*Ber.*, **23**, 2154—2160; compare this vol., p. 1000).—An *azine* of the composition $C_{14}H_9N_3O$ is precipitated in dark-red crystals when pyrroylpyruvic anhydride (*loc. cit.*) is treated with orthophenylenediamine in alcoholic or acetic acid solution. It separates from boiling xylene as a reddish-yellow, crystalline powder, decomposes at about 250°, but without melting, and is only sparingly soluble in alcohol, ethyl acetate, and chloroform, but more readily in boiling xylene, the solutions showing a green fluorescence. It dissolves in concentrated sulphuric acid, forming an intense greenish-blue solution, from which it is reprecipitated on the addition of water. On reduction with zinc and acetic acid, it yields a yellow solution which turns red again on exposure to the air. The *benzoyl*-derivative crystallises in yellow needles, melts at 166° with decomposition, and is soluble in benzene and chloroform, the solutions showing a green fluorescence.

Ethyl anilpyrroylpyruvate, $C_{16}H_{16}N_2O_3$, is formed when ethyl pyrroylpyruvate is warmed with aniline in acetic acid solution. It crystallises from alcohol in long, lemon-yellow needles, melts at 114—115°, and dissolves in concentrated sulphuric acid with a magenta coloration.

Anilpyrroylpyruvic anhydride, $C_{14}H_{10}N_2O_2$, is deposited in yellowish-orange plates when the preceding compound is treated with warm alcoholic ammonia; it can also be prepared by warming pyrroylpyruvic anhydride with aniline in acetic acid solution. It melts at 218°, dissolves in concentrated sulphuric acid with a violet coloration, and does not combine with orthophenylenediamine.

Anilpyrroylpyruvic acid, $C_{14}H_{12}N_2O_3$, is precipitated in crystals when the ethyl salt is treated with cold dilute alcoholic potash, and the aqueous solution of the product acidified. It separates from benzene

in orange crystals, melts at 179° with decomposition, and dissolves in concentrated sulphuric acid with a magenta coloration. Most metallic salts produce a yellow precipitate in an aqueous solution of the ammonium salt.

A compound of the composition $C_{12}H_{11}NO_3$ is obtained when ethyl benzoylpyruvate is heated with hydroxylamine hydrochloride in alcoholic solution; it crystallises from alcohol in large, colourless prisms, melts at 52°, and has the constitution $\begin{matrix} CPh{\cdot}CH \\ \| \qquad\quad \\ N\text{——}O \end{matrix}\!\!>C{\cdot}COOEt$ or $\begin{matrix} CPh{:}CH \\ | \qquad\quad \\ O\text{——}N \end{matrix}\!\!>C{\cdot}COOEt$. The compound formed by the action of hydroxylamine on ethyl pyrroylpyruvate (*loc. cit.*) has probably an analogous constitution. The *acid* prepared from this ethyl salt (m. p. 52°) melts at 162°.

Ethyl pyrrylphenylpyrazolecarboxylate, $C_{16}H_{15}N_3O_2$, prepared by warming ethyl pyrroylpyruvate with phenylhydrazine in glacial acetic acid solution, separates from alcohol in small crystals melting at 168°. The free *acid*, $C_{14}H_{11}N_3O_2$, crystallises from dilute alcohol in long, colourless needles, melts at 215°, and decomposes at a higher temperature. It is readily soluble in alcohol and acetone, but almost insoluble in benzene and light petroleum. In an aqueous solution of the ammonium salt, many metallic salts produce precipitates.

F. S. K.

The Pyrazole-group: Derivatives of Trimethylenephenyldiamine. By L. BALBIANO (*Gazzetta*, **19**, 688—692).—*Trimethylenephenyldiamine*, $NH_2{\cdot}C_3H_6{\cdot}NHPh$.—A solution of 1-phenylpyrazole in absolute alcohol (20 parts) is reduced with metallic sodium, the product distilled and freed from alcohol, and the base extracted with ether and converted into the oxalate. The yield is 45 per cent. The base (obtained from the oxalate) boils constantly at 281—282° (corr.) under a pressure of 758·1 mm.; sp. gr. 0°/0° = 1·0356; 15°/0° = 1·0256. It is soluble in ether and alcohol, but only very moderately in water. A solution in excess of hydrochloric acid is not precipitated by the double iodide of potassium and bismuth. The *succinate* crystallises from alcohol in tufts of large, white, lustrous plates, melts at 100—102° (corr.), and dissolves very readily in cold water, but is insoluble in ether.

Dibenzoyltrimethylenephenyldiamine, $NHBz{\cdot}C_3H_6{\cdot}NPhBz$. — Trimethylenephenyldiamine is quantitatively converted into the benzoyl-derivative by treatment with benzoic chloride and sodium hydroxide in the cold. It thus behaves like the diamines, which have the NH_2 molecules linked to different carbon-atoms (see Udrànszky, Abstr., 1888, 1296). It crystallises in pinkish-white plates, melts at 96·5—97·5°, and is soluble in water, but not in alcohol. *Trimethylenephenyldiamine trimethylenephenylthiocarbamate*,

$$NHPh{\cdot}C_3H_6{\cdot}NH{\cdot}CSSH,NH_2{\cdot}C_3H_6{\cdot}NHPh,$$

is prepared by adding a slight excess of carbon bisulphide to a solution of the base in dilute alcohol and agitating the mixture. A waxy mass separates at first, but is redissolved after boiling for some time. The filtered solution, on cooling, deposits white plates of the new com-

pound which decompose at 116° and are only sparingly soluble in water. With mercuric chloride, the hot aqueous solution yields a white precipitate which is converted into mercuric sulphide by prolonged boiling. The dry mercuric compound decomposes at 210—220°, giving off white fumes which condense to a yellowish liquid having an odour of oil of mustard. S. B. A. A.

Derivatives of Furoïn and Furil. By D. S. MACNAIR (*Annalen*, **258**, 220—230).—*Furoïnphenylhydrazine*,

$$C_4H_3O\cdot CH(OH)\cdot C(N_2HPh)\cdot C_4H_3O,$$

prepared by treating furoïn with phenylhydrazine and a few drops of acetic acid in alcoholic solution, crystallises from a mixture of benzene and light petroleum in colourless needles, melts at 79—81°, and is very readily soluble in alcohol, ether, and benzene, but almost insoluble in water and light petroleum; it rapidly oxidises on exposure to the air, and is readily acted on by hydrochloric acid. The *oxime*, $C_{10}H_9NO_4$, crystallises from alcohol in small, almost colourless prisms, melts at 160—161°, and is readily soluble in hot, but only sparingly in cold, alcohol and benzene; it dissolves freely in soda, yielding a crystalline sodium-derivative.

Deoxyfuroïn, $C_4H_3O\cdot CO\cdot CH_2\cdot C_4H_3O$, can be obtained by treating furoïn with zinc-dust and hydrochloric acid in alcoholic solution, and distilling the product with steam; it melts at 20°, boils at 159—160° (27 mm.), and is only sparingly soluble in water, but readily in ether and alcohol. The *oxime*, $C_{10}H_9NO_3$, crystallises in colourless needles, melts at 94—96°, and is readily soluble in alcohol, ether, benzene, hydrochloric acid, and soda, but only sparingly in water or light petroleum.

Furilphenylhydrazone, $C_4H_3O\cdot CO\cdot C(N_2HPh)\cdot C_4H_3O$, crystallises from boiling light petroleum in orange-yellow needles, melts at 82—83°, and is readily soluble in alcohol, ether, and benzene, but only sparingly in light petroleum and boiling concentrated hydrochloric acid.

Furilphenylosazone, $C_4H_3O\cdot C(N_2HPh)\cdot C(N_2HPh)\cdot C_4H_3O$, prepared by treating furil with phenylhydrazine (2 mols.) in alcoholic acetic acid solution, crystallises from alcohol in yellowish needles, melts at 184°, and is very sparingly soluble in alcohol and light petroleum, but more readily in ether and benzene; it is only very slowly acted on by hot hydrochloric acid.

α-Furiloxime, $C_{10}H_7NO_4$, is formed, together with small quantities of the β-oxime, when furil is treated with hydroxylamine hydrochloride in alcoholic solution at the ordinary temperature. It crystallises from a mixture of benzene and light petroleum in colourless needles, melts at 160°, decomposes at about 200°, and is only sparingly soluble in water and light petroleum, but very readily in most other solvents. When warmed with dilute hydrochloric acid, it is changed into furil. The *β-oxime*, $C_{10}H_7NO_4$, is formed when furil is heated at 100° with an alcoholic solution of hydroxylamine hydrochloride (1 mol.), but a considerable quantity of furil remains unchanged. It separates from water in crystals, melts at 97—98°, and is readily

soluble in alcohol, ether, and benzene, but only sparingly in water and light petroleum; it dissolves in soda, and is decomposed by boiling hydrochloric acid. The *α-dioxime*, $C_{10}H_8N_2O_4$, prepared by treating furil with excess of hydroxylamine hydrochloride as described in the case of the α-oxime, crystallises from hot water in colourless needles containing 1 mol. H_2O, and loses its water of crystallisation at 100°, the anhydrous substance melting at 166—168°. It is very readily soluble in alcohol and ether, but only sparingly in benzene, light petroleum, and water; it dissolves freely in soda, and is decomposed by boiling hydrochloric acid. The *β-dioxime*, $C_{10}H_8N_2O_4$. is obtained when the anhydrous α-dioxime is heated with alcohol at 150—160°; it separates from a mixture of ether and light petroleum in crystals, melts at 188—190° with partial decomposition, and is only moderately easily soluble in ether. F. S. K.

Synthesis of Tetraphenylthiophen. By J. H. ZIEGLER (*Ber.*, **23**, 2472—2476).—The author has previously prepared tetraphenylethylene by the action of sulphur on diphenylmethane (compare Abstr., 1888, 596). Further experiments with benzene-derivatives containing a CH_3- or CH_2-group have shown that the benzene nucleus only reacts with great difficulty, and in exceptional circumstances. *Tetraphenylthiophen* is prepared by heating phenylacetic acid (2 mols.) with sulphur (1 mol.) for six hours at 260°; the product is dissolved in benzene, and, on the addition of alcohol, it crystallises in white needles melting at 181—182°. The same compound is also obtained from deoxybenzoïn by heating with sulphur as above. By the action of concentrated nitric acid on tetraphenylthiophen, a *tetranitro*-derivative is formed. Benzophenone, azobenzene, and triphenylmethane do not react with sulphur at 300°. The author points out that in cases where sulphur combines with the benzene nucleus there is always a basic group present, and this he regards as the reason for the combination taking place; the difference in behaviour of diphenylmethane and triphenylmethane towards sulphur tells, he considers, strongly in favour of his view. The author confirms the conclusions of Pfitzinger and Gattermann regarding the constitution of dehydrothiotoluidine. J. B. T.

Orientation of 4 : 6-Dichlorometaxylene, and on some Derivatives thereof. By A. CLAUS and G. RUNSCHKE (*J. pr. Chem.* [2], **42**, 110—126).—The authors have decided the orientation of the chlorine-atoms in the dichlorometaxylene (m. p. 68°) described by Claus and Burstert (this vol., p. 1105). They did not succeed in obtaining a durene from it by Fittig's reaction, but a dinitro-derivative (see below) can be obtained, which, by conversion into the amido-derivative and oxidation, is converted into a dichlorometaxyloqninone, whose properties show it to be a para-compound; this is conclusive evidence that the dinitro-derivative is a para-compound, and as 2 and 5 are the only possible para-positions in a metaxylene [1 : 3], the chlorine-atoms must have the positions 4 : 6. It is hoped that a general method of orientation may be deduced from the above considerations.

Nitro-4 : 6-*dichlorometaxylene*, obtained by nitrating 4 : 6-dichlorometaxylene with fuming nitric acid in glacial acetic acid at the ordinary temperature, and repeatedly crystallising from alcohol, forms transparent crystals, measurements of which are given; it melts at 118—119°, and is insoluble in the usual solvents. An isomeric nitro-compound has been obtained under somewhat different conditions; it melts at 106° (uncorr.).

Amido-4 : 6-*dichlorometaxylene* is obtained by pouring an alcoholic solution of the nitro-compound little by little into a solution of stannous chloride in strong hydrochloric acid and warming for 3—4 hours on the water-bath; the *stannochloride* crystallises on cooling and may be decomposed by aqueous potash. It forms colourless needles, which soon become coloured, melts at 85° (uncorr.), and dissolves in the usual solvents. Its *hydrochloride* and *platinochloride* have been obtained. The amido-derivative corresponding with the nitro-derivative melting at 106° melts at 72° (uncorr.).

2 : 5-*Dinitro*-4 : 6-*dichlorometaxylene* is prepared by adding the dichloroxylene (1 part) in small quantities to a mixture (5 parts) of 1 part of fuming nitric acid (sp. gr. 1·52) and 2 parts of sulphuric acid, and pouring the mixture into water after a day; it separates in yellow flocks, which are washed with hot alcohol to dissolve the nitro-derivative. It crystallises from chloroform in pale-yellow cubes, melts at 223° (uncorr.), and dissolves freely in chloroform and glacial acetic acid. When it is suspended in alcohol and acted on with stannous chloride, it yields 2 : 5-diamido-4 : 6-dichlorometaxylene. This crystallises in dazzlingly white prisms or needles when pure, but the crystals are generally yellowish or rosy; it melts at 176° (uncorr.); the *hydrochloride*, *sulphate*, and *platinochloride* are described.

Dichlorometaxyloquinone is obtained by oxidising the diamido-compound in dilute glacial acetic acid solution with dilute aqueous chromic acid; it crystallises in large, pretty, sulphur-yellow leaves which melt at 178° (uncorr.), sublime, and dissolve in the usual solvents. By reduction with stannous chloride it yields *dichlorometaxyloquinol* (dichlorodimethylquinol) [$Me_2 : Cl_2 : (OH)_2$ = 1 : 3 : 4 : 6 : 2 : 5], which crystallises in slender, colourless needles melting at 224° (uncorr.), and soluble in the usual solvents.

2 : 5-*Dibromo*-4 : 6-*dichlorometaxylene* is formed when 4 : 6-dichlorometaxylene is treated with bromine (4 atoms) and iron in glacial acetic acid for some days and water added. It crystallises from ether, benzene, &c., in long, brilliant, white, silky needles which melt at 230° (uncorr.), and can be sublimed. If only 2 atoms of bromine are employed, the same dibromo-compound is formed and half the dichloro-compound remains unchanged. A. G. B.

Dibromoxylenes and Dichloroxylenes, and their Transformations by means of Sulphuric Acid. By E. Koch (*Ber.*, 23, 2318—2321).—Solid dibromoxylene [$Me_2 : Br_2$ = 1 : 4 : 2 : 5], when heated with concentrated sulphuric acid at 215°, yields a liquid isomeride boiling at 260—265°, probably [1 : 4 : 2 : 3]. Under similar circumstances the solid 1 : 2 : 4 : 5-compound yields the isomeric 1 : 2 : 3 : 4-compound, boiling at 275—280°.

By the action of chlorine and iodine on cold metaxylene, two dichlorinated derivatives are obtained. One is a solid, melting at 68·5° and boiling at 223—224°. When treated with methyl iodide and sodium, it yields durene, and has therefore the formula [Me_2 : Cl_2 = 1 : 3 : 4 : 6]. By treatment with chlorosulphonic acid it yields a sulphonic acid of the formula [Me_2 : Cl_2 : SO_3H = 1 : 3 : 4 : 6 : 2]. The sodium salt forms white plates, the potassium salt white needles, and both are soluble in water; the calcium and barium salts form brilliant, white plates, only sparingly soluble in water. The amide forms small plates melting with decomposition above 250°. The other dichlorometaxylene is a liquid solidifying at −20° and boiling at 221·5°. It is convertible into prehnitene and has therefore the formula [Me_2 : Cl_2 = 1 : 3 : 2 : 4]. The sulphonic acid has the formula [Me_2 : Cl_2 : SO_3H = 1 : 3 : 2 : 4 : 6]. The potassium and sodium salts form brilliant needles very soluble iu water, the calcium and barinm salts very sparingly soluble, shining plates. The amide forms small, white plates melting with decomposition above 300°. The constitution of the sulphonic acids was determined by means of the metaxylenesulphonamides which they yield when treated with zinc-dust and ammonia. When the solid dichloroxylene is heated with strong sulphuric acid at 220°, about 12 per cent. is changed into the liquid isomeride.

Dibromodichloroxylene [Me_2 : Cl_2 : Br_2 = 1 : 3 : 2 : 4 : 5 : 6], obtained by the action of bromine on cold dichloroxylene, crystallises from acetic acid in brilliant, silky needles melting at 215°, and scarcely soluble in alcohol.

Dinitrodichloroxylene [Me_2 : Cl_2 : $(NO_2)_2$ = 1 : 3 : 2 : 4 : 5 : 6], obtained by adding dichloroxylene to a warm mixture of nitric and snlphuric acids, crystallises from alcohol in brilliant, pale-yellow needles melting at 155°.

Dinitrodichloroxylene [1 : 3 : 4 : 6 : 2 : 5], obtained as above from the corresponding dichloroxylene, crystallises from acetic acid and alcohol in short, hard prisms melting at 215°.

Tetrachlorometaxylene, formed together with symmetrical dichlorometaxylene when metaxylene is chlorinated, crystallises from acetic acid in flexible needles melting at 212°.

A solid *dichlororthoxylene* is formed in small quantity in addition to a liquid isomeride when orthoxylene is chlorinated. It crystallises from alcohol in long, hard needles melting at 73°. C. F. B.

Laurenes. By E. Uhlhorn (*Ber.*, **23**, 2346—2349).—On distilling camphor with zinc chloride, a considerable quantity of liquid is obtained, boiling at 180—200°, which is known to be a mixture of various hydrocarbons. From the fraction boiling at 183—184·5°, derivatives of ethylxylene [Me : Me : Et = 1 : 2 : 4] are obtained. The portion boiling at 188—190° yields derivatives of ethylxylene [Me : Me : Et = 1 : 4 : 5]. The intermediate fraction boiling at 185—187° in all probability consists of ethylxylene [Me : Me : Et = 1 : 3 : 4]. From the portions boiling at 190—192°, a mixture of the barium sulphonates of the first two ethylxylenes is obtained, together with a resinous, amorphous salt. The various compounds serving for

identification were in all cases compared with synthetical specimens. These results are in accordance with the observations of Armstrong and Miller (compare Abstr., 1884, 43). J. B. T.

Propylxylenes. By E. UHLORN (*Ber.*, **23**, 2349—2351).—Propylorthoxylene [Me : Me : Pr^{α} = 1 : 2 : 4] is prepared from bromorthoxylene and propyl bromide; it boils at 209° and does not solidify at −20. The *sulphonic acid* crystallises in slender needles. The *barium sulphonate*, $(C_{11}H_{15}SO_3)_2Ba + 3\frac{1}{2}H_2O$, forms nodular crystals. The *magnesium* salt, $(C_{11}H_{15}SO_3)_2Mg + 5H_2O$, crystallises in plates. The *sodium sulphonate*, $C_{11}H_{15}SO_3Na + H_2O$, is deposited in lustrous prisms. *Propylorthoxylenesulphonamide* crystallises in needles melting at 123—124°. The *sulphanilide* forms interlaced needles and melts at 213—214°. *Tribromopropylorthoxylene* is obtained in long, white needles melting at 48°.

Propylmetaxylene [Me : Me : Pr^{α} = 1 : 3 : 4] boils at 208—208·5° and remains liquid at −20. The *sulphonic acid* crystallises in groups of needles. The *barium salt*, $(C_{11}H_{15}SO_3)_2Ba + 2H_2O$, forms needles; the *magnesium salt*, $(C_{11}H_{15}SO_3)_2Mg + 5H_2O$, is deposited in thin, colourless plates; the *sodium salt*, $C_{11}H_{15}SO_3Na + 4\frac{1}{2}H_2O$, crystallises in long, transparent needles. *Propylmetaxylenesulphonamide* is obtained in needles melting at 102°. The *sulphanilide* melts at 180—182°. The *trinitro-* and *tribromo-*derivatives crystallise in needles, and melt at 110° and 39° respectively.

Propylparaxylene [Me : Me : Pr^{α} = 1 : 4 : 5] boils at 206—207°, and does not solidify at −20°. The *sulphonic acid* crystallises in needles. The *barium salt* forms anhydrous, lustrous tables. The *sodium salt*, $C_{11}H_{15}SO_3Na + 1\frac{1}{2}H_2O$, is readily soluble in water, and is deposited in lustrous needles. *Propylparaxylenesulphonamide* crystallises in thin plates melting at 124·5°. The *sulphanilide* is obtained in rhombic crystals melting at 215—216°. The *trinitro-derivative* melts at 85°, and the *tribromo-compound* at 49°; both crystallise in needles.

Isopropylmetaxylene [Me : Me : Pr^{β} = 1 : 3 : 4] is prepared by treating paraisocymene with bromine and methyl bromide successively; it boils at 194—195°. The *sulphonic acid* crystallises in prisms. The *barium sulphonate* is readily soluble in water, and is deposited in spear-shaped needles. The *sodium sulphonate*, $C_{11}H_{15}SO_3Na + 4H_2O$, forms long, slender needles. The *sulphonamide* melts at 163°; the *sulphanilide* at 207°; the *tribrominated* derivative at 261°; and the *trinitro*-derivative at 182°; all four compounds crystallise in needles.

J. B. T.

Orthocyanobenzyl Chloride. By A. W. DAY and S. GABRIEL (*Ber.*, **23**, 2478—2489).—It is well known that ortho-derivatives of benzonitrile, containing a hydroxyl-group in the side chain, readily undergo rearrangement, with formation of the group ·C:NH·O·. The same property is shown by the corresponding mercaptan-derivatives. *Orthocyanobenzyl thiocyanate*, $CN·C_6H_4·CH_2·SCN$, is prepared by boiling orthocyanobenzyl chloride with an alcoholic solution of potassium thiocyanate for about two hours; on pouring the solution into water an oil separates, which solidifies, and, after some time,

is purified by washing with water and dilute alcohol; 15·5 grams of cyanobenzyl chloride yield 16—17 grams of the thiocyanate. The compound crystallises from dilute alcohol in colourless needles melting at 86°. By the action of concentrated hydrochloric acid on the thiocyanate at 180°, thiophthalide is obtained; it has previously been prepared by Graebe (compare Abstr., 1889, 140) by the action of an alkaline hydrogen sulphide on nitrosophthalimidine, and has the second of the proposed formulæ, namely, $C_6H_4<\substack{CO \\ CH_2}>S$ (see below). Cyanobenzyl thiocyanate is dissolved in concentrated sulphuric acid, and the solution heated, first at 30—50°, and finally at 60—70°; on pouring into water and adding ammonia, an oily liquid separates and solidifies on cooling. It is soluble in alcohol and ether, and crystallises from light petroleum in small, white needles melting at 62°, and becoming brown on exposure to air. This compound affords a striking instance of tautomerism; it reacts both as *orthocyanobenzyl mercaptan*, $CN\cdot C_6H_4\cdot CH_2\cdot SH$, and as *thiophthalimidine*, $C_6H_4<\substack{C:NH \\ CH_2-}>S$. The same substance is also obtained by the action of the calculated quantity of alcoholic potassium hydrosulphide on orthocyanobenzyl chloride; after remaining for an hour the liquid is treated with hydrochloric acid, the alcohol removed, and the compound precipitated with ammonia from an aqueous solution (see below). By the action of sodium hydroxide on this compound, ammonia is eliminated, and thiomethylbenzoic acid is formed, which yields thiophthalide on boiling with water.

Derivatives of Thiophthalimidine.—In the following reactions the compound C_8H_7NS behaves as if it were thiophthalimidine. The *platinochloride*, $(C_8H_7NS)_2,H_2PtCl_6$, crystallises in orange-yellow prisms. The *picrate* is deposited in slender needles. The *hydrochloride* dissolves very readily in water, and is partly decomposed on evaporating the solution; it crystallises in white needles. The *hydriodide* is obtained in colourless needles, which decompose at 100°.

Methylthiophthalimidine, $C_6H_4<\substack{C(NMe) \\ CH_2-S}>$, is prepared by dissolving thiophthalimidine in excess of methyl iodide: after remaining for 1—2 hours the crystals of thiophthalimidine hydriodide are separated, and the residue distilled in a current of steam; on extracting the distillate with ether, and evaporating the latter, a yellow, basic oil remains, which decomposes on heating. The yield is one-third of the theoretical. The *hydrochloride*, $C_8H_6Me\cdot NS,HCl$, is stable at 100°; the *platinochloride* forms a sparingly soluble, brownish-yellow, crystalline powder; the *picrate* crystallises in yellow needles. The constitution of the base is shown by the formation of thiophthalide and methylamine on heating it with concentrated hydrochloric acid at 180—190° for five hours.

In the following reactions the compound C_8H_7NS behaves like *orthocyanobenzyl mercaptan*. *Methyl orthocyanobenzyl sulphide*, $CN\cdot C_6H_4\cdot CH_2\cdot SMe$, is formed by the action of methyl iodide on an alkaline solution of the mercaptan; it is a pale-yellow, viscid liquid, boiling at 278° under a pressure of 757 mm., and does not show basic

properties; by the action of concentrated hydrochloric acid at 100°, ammonia is eliminated, and *methylbenzylsulphide-orthocarboxylic acid*, $COOH{\cdot}C_6H_4{\cdot}CH_2{\cdot}SMe$, is formed. *Diorthocyanobenzyl disulphide*, $CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}S_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}CN$, is prepared by the action of potassium ferrocyanide on an alkaline solution of the mercaptan. It crystallises from alcohol in long prisms which melt at 124°. On heating it with concentrated hydrochloric acid at 160°, ammonia, sulphuric acid, and thiophthalide are formed; it is probable, however, that in the first instance, a dicarboxylic acid, $COOH{\cdot}C_6H_4{\cdot}CH_2{\cdot}S_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}COOH$, is produced, and that this decomposes into thiophthalide, water, and oxygen.

In addition to the compound C_8H_7NS (see above), a substance of the formula $C_{16}H_{10}S_3$ is formed by the action of excess of alcoholic potassium hydrosulphide (3—4 mol. proportions) on orthocyanobenzyl chloride (comp. this vol., p. 1221). The compound is deposited in small, flat needles, which appear brown by transmitted light, and have a metallic dark-green tint in reflected light; it is very sparingly soluble in ordinary media, but may be recrystallised from nitrobenzene. With concentrated sulphuric acid, a magenta colour is obtained, and on adding water the compound is precipitated seemingly unchanged. The same substance is formed by the action of alcoholic potassium hydrosulphide on thiophthalimidine.

Diorthocyanodibenzylamine, $(CN{\cdot}C_6H_4{\cdot}CH_2)_2NH$, is prepared by dissolving orthocyanobenzyl chloride in a 10 per cent. alcoholic solution of ammonia; after remaining for about six days at the ordinary temperature, the crystals which form are separated, washed with alcohol, and decomposed with sodium hydroxide. It crystallises from water in slender needles, melts at 125°, and is readily soluble in alcohol. The *hydrochloride* is deposited in needles; the *platinochloride* forms a yellowish-red, crystalline powder. On evaporating the ammoniacal mother liquors obtained in the preparation of the above base, crystals of orthocyanobenzylamine hydrochloride are deposited; this compound has already been described. J. B. T.

Benzoyl-derivatives of Acetonitrile. By E. v. MEYER (*J. pr. Chem.* [2], **42**, 267—269).—Monobenzoylacetonitrile or cyanacetophenone is obtained from imidobenzoylcyanomethyl (Abstr., 1888, 683) by shaking it with hydrochloric acid. The precipitate, on solution in ethyl acetate and addition of light petroleum, forms snow-white needles melting at 80·5—81°, and agrees in all its properties with the cyanacetophenone described by Haller (Abstr., 1889, 473).

If a mixture of acetonitrile and benzoic chloride be treated with sodium in ethereal solution, *dibenzoylacetonitrile*, $CBz_2H{\cdot}CN$, is formed, together with methane, sodium cyanide, and other organic sodium salts The precipitate, after washing with ether, is dissolved in water, the solution extracted with ether, and acidified with sulphuric acid. The voluminous precipitate is then recrystallised from alcohol, and forms silky needles melting at 156·5°. It readily yields a silver salt. Towards alkalis it is exceptionally stable, but it is decomposed on warming with moderately dilute sulphuric acid, with formation of carbonic anhydride, acetophenone, benzoic acid, and ammonia. On

warming the silver salt with methyl iodide, a compound was obtained, crystallising from ethyl acetate in lustrous needles which melted at 214°, and were insoluble in dilute ammonia. The quantity was, however, too small to determine whether it was the *methyl* ether, $CBz_2Me·CN$.

Further investigation is also necessary to determine whether dibenzoylacetonitrile has the constitution assigned to it above, as its properties agree equally well with the formula $OH·PhC:CBz·CN$.

H. G. C.

Tricyanides. By F. KRAFFT and G. KOENIG (*Ber.*, **23**, 2382—2388; compare Abstr., 1889, 696).—Methyl diphenyl tricyanide is best prepared by pouring the product obtained from the action of aluminium chloride on benzonitrile and acetic chloride into ice-cold water, and distilling the insoluble portion in a current of steam; the residue is finely ground, treated with dilute sodium hydroxide solution, washed with water, and recrystallised from alcohol.

Diphenyltricyanocarboxylic acid, $C_3N_3Ph_2·COOH$, is obtained by boiling methyldiphenyl tricyanide for 12 to 15 hours with potassium permanganate in alkaline solution; the product is filtered hot, the manganese precipitate boiled with water, and the solution, when nearly cold, treated with hydrochloric acid. The acid, which separates as a voluminous precipitate, crystallises from dilute alcohol in slender, thin, lustrous prisms melting at 192° with decomposition. The *potassium salt* crystallises in long, slender, lustrous needles, very sparingly soluble in water. *Hydrogen diphenyl tricyanide*, $C_3N_3HPh_2$, is obtained by heating the carboxylic acid at about 192°; it melts at 75°, boils at 205° at 9 mm., and is readily soluble in dilute alcohol.

Caprylic chloride, $C_7H_{15}·COCl$, is prepared by the action of phosphorus pentachloride on caprylic acid at 0°; it boils at 83° at 15 mm. *Heptyl diphenyl tricyanide*, $C_3N_3(C_7H_5)Ph_2$, is obtained by the action of aluminium chloride on benzonitrile and caprylic chloride; it crystallises from alcohol in lustrous leaves melting at 28°, and boiling at 274—275° under a pressure of 15 mm.

Nonylic chloride, $C_7H_{17}·COCl$, is formed from nonylic acid and phosphorus pentachloride; it is a colourless liquid, boiling at 98° under a pressure of 15 mm.; on exposure to moist air it slowly undergoes decomposition. *Octyl diphenyl tricyanide*, $C_3N_3(C_8H_{17})Ph_2$, is prepared from nonylic chloride; it is purified by recrystallisation from alcohol, melts at 43°, and boils at 284—285° under a pressure of 15 mm.

Capric chloride, $C_9H_{19}·COCl$, is obtained from capric acid; it boils at 114° under a pressure of 15 mm., and rapidly decomposes on exposure to air. *Nonyl diphenyl tricyanide*, $C_3N_3(C_9H_{19})Ph_2$, is formed from capric chloride; it may be crystallised from alcohol; it melts at about 38°, and boils at 292—294° under a pressure of 15 mm. A comparison of the melting points of this series of tricyanides with those of the normal fatty acids shows the same regularity. The melting points of tricyanides obtained from acids with an even number of carbon-atoms follow a curve, and, in the case of the whole series, they rise and fall periodically from member to member. In contrast to this, the boiling points steadily rise with increasing molecular weight.

Methyl diparatoluyl tricyanide, $C_3N_3Me(C_6H_4Me)_2$, is prepared from paratoluonitrile and acetic chloride; it is very sparingly soluble in alcohol, but crystallises from isobutyl alcohol in small, lustrous needles melting at 159°, and boiling at 245° under a pressure of 15 mm.; the yield is large.

The chlorides of the bibasic acids condense to form tricyanide-derivatives in a similar manner to those of the monobasic acids. *Ethylene tetraphenyl hexacyanide*, $C_3N_3Ph_2 \cdot CH_2 \cdot CH_2 \cdot C_3N_3Ph_2$, is obtained from benzonitrile and succinic chloride by heating with aluminium chloride on the water-bath for several days; the product is washed with ice-cold water, and extracted several times with ether; after evaporation, the residue is dissolved in nitrobenzene, and, on cooling, it crystallises in slender, lustrous plates which melt about 245°.

J. B. T.

Action of Benzoic Chloride on Sodium Cyanamide in the Presence of Ether. By W. BUDDÉUS (*J. pr. Chem.* [2], **42**, 82—109).—Gerlich (this Journal, 1876, ii, 196) did not succeed in producing benzoylcyanamide by the action of benzoic chloride on sodium cyanamide in molecular proportion, and in ethereal solution. The author finds that sodium cyanamide (2 mols.) acts on benzoic chloride (1 mol.) in ether with the formation of sodium benzoylcyanamide, cyanamide, and sodium chloride.

Benzoylcyanamide, $NHBz \cdot CN$, is obtained from the sodium compound by the action of mineral acids; it melts at 126°, at the same time becoming yellow, and decomposing with the formation of benzonitrile, carbonic anhydride, and dicyanodiamide; it is not precipitated from its metallic compounds by organic acids, so that sodium acetate solution easily dissolves it; its solution in water is strongly acid, and its metallic compounds are neutral. Benzoylcyanamide is not polymerised by heat, either by itself or in liquids of high boiling point; when heated with an alcohol, it yields the corresponding benzoate and cyanamide. The metallic compounds of benzoylcyanamide are easily soluble in water and alcohol, except the silver compound. The *barium compound*, $Ba(NBz \cdot CN)_2,H_2O$, when heated, decomposes into benzonitrile, carbonic anhydride, and barium cyanamide; the *sodium*, *potassium*, *ammonium*, *copper* (with 2 mols. H_2O), *lead*, and *silver* compounds are also described.

The product of the action of sodium cyanamide on benzoic chloride in molecular proportion, dissolved in ether, after being washed, first with ether and then with water, leaves a yellow mass, which contains two isomeric compounds of the formula $(C_7H_4N_2)_x$. The other products formed by this treatment are carbonic anhydride, hydrogen cyanide, benzonitrile, cyanamide, sodium chloride, dibenzoylcyanamide, and asymmetrical dibenzoylcarbamide.

The *asymmetrical dibenzoylcarbamide*, $NBz_2 \cdot CO \cdot NH_2$, is produced by the action of water on the dibenzoylcyanamide contained in the residue left on evaporating the yellow ethereal solution; it crystallises from alcohol in slender, white needles which melt at 197°, whereas symmetrical dibenzoylcarbamide melts at 210°.

The *compounds*, $(C_7H_4N_2)_x$, left in the yellow mass after treatment

with water, are recrystallised from phenol, when one of them separates in the form of brilliant, long, yellow needles; the other crystallises from the mother liquor in short, well-formed, hexagonal and rhombic prisms. From about 800 grams of sodium cyanamide, 20 to 30 grams of the needles and 5 grams of the prisms were obtained. These compounds do not melt at 360°, but sublime unchanged at a red heat; they are unchanged even by prolonged heating with fuming nitric acid; they are insoluble in the usual solvents, but dissolve in liquids of high boiling point, such as phenol, aniline, nitrobenzene, quinoline, and benzonitrile.

Gerlich (*loc. cit.*) obtained a substance by the dry distillation of tribenzoylmelamine, which he termed pseudotriphenylmelamine, and to which he ascribed the formula $(C_7H_6N_2)_x$. The author believes that this substance is identical with those described above, and that Gerlich's formula is wrong. The investigation of these substances is being continued. A. G. B.

Orthamidobenzyl Alcohol. By H. G. Söderbaum (*Ber.*, **23**, 2183—2187; compare Söderbaum and Widman, this vol., p. 178).—When phenomethyldihydroketometadiazine is oxidised with chromic acid in glacial acetic acid solution, it is converted into γ-methylbenzoylenecarbamide (m. p. 234°), identical with the compound prepared by Abt (Abstr., 1889, 609) from orthamidomethylbenzamide and carbamide. This same substance is also formed when phenomethyldihydroketothiometadiazine is oxidised with potassium permanganate.

Phenoethyldiketometadiazine (*γ-ethylbenzoylenecarbamide*),

$$C_6H_4<\begin{matrix}CO\cdot NEt \\ \mid \\ NH\cdot CO\end{matrix},$$

can be obtained by oxidising phenoethyldihydrothiometadiazine with potassium permanganate and decomposing the crystalline potassium salt produced in this way with acetic acid. It crystallises from boiling alcohol in colourless needles or plates, melts at 195°, and resembles the corresponding methyl-derivative in its behaviour with solvents; its solution in alcoholic potash shows a bluish-violet fluorescence. F. S. K.

Action of Chromyl Dichloride on Cymene. By G. Errera (*Gazzetta*, **19**, 528—532; compare Abstr., 1880, 467; 1881, 423—581; 1884, 312).—When the product of the action of chromyl dichloride on cymene is decomposed with water, two isomeric compounds, having the formula $C_6H_4Me\cdot C_3H_5O$, are obtained; one of these combines with the hydrogen sulphites, and appears to be identical with Richter and Schüchner's paramethylhydrocinnamaldehyde (Abstr., 1884, 1342), but does not form crystals on prolonged exposure to the air; its aldehydic character is, however, shown by its conversion into an *alcohol*, $C_6H_4Me\cdot C_3H_6\cdot OH$, by the action of nascent hydrogen. This alcohol boils at 237—239°, and yields with hydrochloric acid the corresponding *chloride*, $C_6H_4Me\cdot C_3H_6Cl$, boiling at 225—230°; the latter, on being boiled with acetic acid and silver acetate, is converted into

the *acetate*, $C_6H_4Me\cdot C_3H_6\cdot OAc$, which boils at 240—245°; by treatment with alcoholic potash, the unsaturated hydrocarbon, $C_6H_4Me\cdot C_3H_5$, boiling at 198—200, is formed. This hydrocarbon appears to be identical or isomeric with the α-paratolylpropylene previously described by the author (Abstr., 1885, 655).

The other isomeride boils at 222—226°, and does not combine with the hydrogen sulphites; a somewhat unstable *phenylhydrazone* of this substance, $C_6H_4Me\cdot C_3H_5\!:\!N_2HPh$, melting at 75°, a *nitro-derivative*, $NO_2\cdot C_6H_3Me\cdot C_3H_5O$, melting at about 60°, and the phenylhydrazine compound of the latter, $NO_2\cdot C_6H_3Me\cdot C_3H_5\!:\!N_2HPh$, melting at 127—128°, have also been prepared. S. B. A. A.

Action of Chlorine on Catechol and Orthamidophenol. By T. ZINCKE and F. KÜSTER (*Ber.*, **23**, 2200—2225).—It has been previously shown (this vol., p. 754) that $\gamma\gamma$-hexachlorohydroxypentenecarboxylic acid, on oxidation, gives a ketone (m. p. 92°) isomeric with the ketone (m. p. 31°) obtained from the corresponding $\beta\gamma$-acid (Abstr., 1888, 1278) in like manner; the course of the reaction depends, however, on the nature of the oxidising agent employed, as will be seen from the experiments described below.

$\gamma\gamma$-Hexachloroketopentene (m. p. 92°) is obtained, together with about an equal quantity of a compound of the composition $C_{10}Cl_{10}O_3H_2$, when $\gamma\gamma$-hexachlorohydroxypentenecarboxylic acid (m. p. 186°) is oxidised with chromic acid in the manner previously described in the case of the isomeric acid (m. p. 111°). The hot solution is diluted with water, and the two oxidation-products, which are precipitated, separated by recrystallisation from benzene, in which the ketone only is moderately easily soluble. $\gamma\gamma$-Hexachloroketopentene is precipitated in crystals, together with traces of a substance melting at 173°, when chlorine is passed into a warm aqueous solution of the $\gamma\gamma$-acid; the yield is almost theoretical. It is also formed when the $\gamma\gamma$-acid is oxidised with chlorine in dilute acetic acid solution, or with sodium hypochlorite and glacial acetic acid, but oily bye-products are also obtained in these reactions.

$\gamma\gamma$-Hexachloroketopentene forms large, colourless, transparent, monosymmetric crystals, $a:b:c = 0.60339:1:0.73795$, $\beta = 64°\ 43'$, melts at 92°, and boils at 148° (75 mm.), and at 235·5° (740·5 mm.); it sublimes in plates, is readily volatile with steam, and has an odour recalling that of camphor and chloroform; it is readily soluble in benzene, chloroform, and ether, crystallises well from alcohol and glacial acetic acid, and separates unchanged from boiling concentrated nitric acid in colourless needles. It does not react with hydroxylamine, but it gradually combines with aniline in cold benzene solution, yielding a brown, amorphous substance; it is slowly acted on by sodium carbonate in alcoholic solution, yielding a resinous substance, which is precipitated on the addition of an acid. Alkalis convert it into resinous acids, even at the ordinary temperature; in the cold, a very small quantity of pentachloropentolic acid (pentachlorobutenecarboxylic acid, Abstr., 1888, 1278) and larger quantities of an unstable isomeric acid are produced.

γγ-Pentachlorobromoketopentene, C_5Cl_5BrO, is formed when an aqueous solution of the γγ-acid (10—15 grams) is heated with bromine (25—30 grams) and hydrobromic acid (20 grams) until no further action takes place, but part of the acid remains unchanged; the ketone, which is deposited from the cold solution in crystals, is separated by filtration, treated with light petroleum to free it from the unchanged acid, and the clear solution evaporated. It is best prepared by heating the γγ-acid with a slight excess of the theoretical quantity of sodium hypobromite in glacial acetic acid solntiou, the product being purified in the manner just described. It is also formed when the βγ-acid is oxidised with bromine or sodium hypobromite, a βγ-ketone of the composition C_5Cl_5BrO not being obtained under these conditions; it is best prepared from the βγ-acid by heating it at 100° in sealed tubes for 1—1½ hours with bromine (5 parts) and water (5 parts). The ketone obtained from the βγ-acid by oxidation with chlorine is identical with the compound (m. p. 31°) obtained by oxidation with chromic acid (Abstr., 1888, 1278), and the formation of a γγ-ketone could not be detected under these conditions.

Pentachlorobromoketopentene forms monosymmetric crystals, $a : b : c = 0{\cdot}60930 : 1 : 0{\cdot}75765$, $\beta = 64°\ 57\frac{1}{2}'$, identical in appearance with those of the hexachloro-compound; it melts at 102°, its sp. gr. is 2·159 at 15°, and it has an odour like that of the hexachloroketone, which it also resembles very closely in chemical behaviour. It dissolves in well-cooled soda, yielding the sodium salt of an unstable acid of the composition $C_5Cl_4Br{\cdot}COOH$ and a stable compound which seems to be a mixture of pentachloropentolic acid (m. p. 127°) aud bromotetrachloropeutolic acid; its behaviour with sodium carbonate and hydroxylamine is the same as that of the hexachloroketone, but it is not acted on by hydrocyanic acid, and it is not converted into the corresponding βγ-ketone on heating, decomposition taking place at the temperature required. Its constitution is expressed by the formula $\begin{matrix}CBr{\cdot}CCl_2\\ \| \\ CCl{\cdot}CCl_2\end{matrix}\!\!>\!CO$.

When βγ-hexachloroketopentene is heated at 290—300°, it is partially converted into the γγ-ketone, the latter, under the same conditions, undergoing transformation into the βγ-compound; when the βγ-ketone is heated with hydrochloric acid and manganese dioxide at 120° in sealed tubes, it is almost completely converted into the isomeride.

γγ-Octochloropentene, $\begin{matrix}CCl{\cdot}CCl_2\\ \| \\ CCl{\cdot}CCl_2\end{matrix}\!\!>\!CCl_2$ (this vol., p. 755), crystallises from light petroleum in thick, colourless prisms, melts at 41°, boils at 283°, and is readily soluble in the ordinary solvents; it is not acted on by alkalis, and it is only very slowly destroyed by concentrated nitric acid.

γγ-Hexachloro-α-hydroxypentene cyanide, $\begin{matrix}CCl{\cdot}CCl_2\\ \| \\ CCl{\cdot}CCl_2\end{matrix}\!\!>\!C(OH){\cdot}CN$, is obtained when the γγ-ketone is treated with potassium cyanide in well-cooled alcoholic solution, and the salt thus produced decomposed

with dilute hydrochloric acid. It crystallises from hot light petroleum in colourless needles, melts at 128°, and decomposes at about 150° into ketone and hydrogen cyanide; it is readily soluble in alcohol, ether, chloroform, benzene, and light petroleum, and it seems to crystallise unchanged from hot concentrated nitric acid, but it is decomposed by warm water, warm dilute hydrochloric acid. and boiling acetic anhydride. It dissolves unchanged in dilute alkalis, yielding the corresponding alkaline-derivative, and it is not converted into a hydroxy-acid when boiled with 10 per cent. soda, or when heated with hydrochloric or sulphuric acid in alcoholic solution. The *acetyl*-derivative, $C_6Cl_6(OAc)\cdot CN$, prepared by heating the cyanide with acetic chloride at 120—130°, crystallises from benzene in large, colourless, hexagonal prisms, melts at 96—97°, and is decomposed by boiling alkalis, water, and dilute hydrochloric acid, being converted into the ketone.

The *amide*, $\begin{matrix} CCl\cdot CO \\ \| \\ CCl\cdot CCl_2 \end{matrix}\!\!>\!C(OH)\cdot CO\cdot NH_2$, is formed, with evolution of hydrogen chloride, when $\gamma\gamma$-hexachloroketopentene is warmed for a short time with concentrated sulphuric acid. It separates from ether in long, colourless needles, melts at 198—200° with decomposition, and is very readily soluble in alcohol and ether, and moderately easily in benzene, but only sparingly in light petroleum; it crystallises unchanged from dilute hydrochloric acid and from concentrated nitric acid, and it dissolves in alkalis with evolution of ammonia.

Pentachloropentolamide, $CCl_2{:}CCl\cdot CCl{:}CCl\cdot CO\cdot NH_2$, is formed when $\gamma\gamma$-hexachloroketopentene is dissolved in benzene, the solution saturated with anhydrous ammonia in the cold, and kept for 12 hours at the ordinary temperature (compare this vol., p. 755). It separates from a mixture of ether and light petroleum in compact crystals, and from a mixture of benzene and light petroleum in quadratic plates or prisms, melts at 116°, and is readily soluble in ether, benzene, and alcohol, but more sparingly in light petroleum; it dissolves in hot dilute soda with evolution of ammonia, and on acidifying the solution, pentachloropentolic acid (m. p. 127°) is precipitated in crystals.

The compound of the composition $C_5Cl_5H_2N_2O$ (compare this vol., p. 755), which is obtained by treating $\beta\gamma$-hexachloroketopentene with ammonia under the same conditions as those described in the case of the $\gamma\gamma$-ketone, crystallises from a mixture of ether and light petroleum in large, colourless prisms, from hot benzene in rhombic plates melting at 118°, and from hot water in long needles melting at 127°. It is readily soluble in alcohol and ether, but only moderately easily in benzene, and sparingly in light petroleum; it dissolves in alkalis, yielding a solution which has a strong odour of carbylamine, but it is not acted on by boiling acetic anhydride, acetic chloride, nitrous acid, or warm concentrated sulphuric acid. Phosphoric chloride, at 180—190°, converts it into a very unstable, crystalline substance which contains phosphorus, and which is reconverted into the original compound when treated with water. F. S. K.

Alkylation of Formanilide. By W. J. COMSTOCK (*Ber.*, **23**, 2274—2275).—Silver formanilide reacts very readily with an ethereal solution of iodine, giving formopariodoanilide, C_7H_6NOI, and also with methyl iodide, yielding methylisoformanilide, NPh:CH·OMe. Since sodioformanilide reacts with methyl iodide to form methylformanilide, it must have the constitution NPhNa·CHO; silver formanilide, on the other hand, must have the constitution NPh:CH·OAg.

When dry silver succinimide is treated with methyl iodide, an oil, which boils at about the same temperature as methylsuccinimide, is obtained; this compound, unlike methylsuccinimide, combines with aniline in the cold, yielding a solid basic product.

A full account of the author's experiments will be published in the *American Chemical Journal.* F. S. K.

Phenylorthobenzylenediamine and Paratolylorthobenzylenediamine. By H. G. SÖDERBAUM and O. WIDMAN (*Ber.*, **23**, 2187—2195).—*Orthamidobenzylparatoluidine*,

$$NH_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot C_6H_4Me,$$

can be obtained by reducing the corresponding nitro-compound with zinc-dust and glacial acetic acid; it crystallises from alcohol in thin, quadratic plates, melts at 80·5°, and is readily soluble in benzene, chloroform, and alcohol, but almost insoluble in light petroleum. The *diacetyl*-derivative, $NHAc\cdot C_6H_4\cdot CH_2\cdot NAc\cdot C_6H_4Me$, prepared by boiling the base with acetic anhydride, crystallises in colourless plates, melts at 185—186°, and is sparingly soluble in ether and hot alcohol.

The authors tried repeatedly to prepare the paratolylbenzylene-ethenylamidine described by Lellmann and Stickel (Abstr., 1886, 793), but without success; when the acetyl-derivative of orthonitrobenzylparatoluidine (m. p. 65°) is reduced with tin and hydrochloric acid in glacial acetic acid, as described by Lellmann and Stickel, it yields very small quantities of a substance which is difficult to purify, so that the supposed amidine is most probably nothing but impure orthamidobenzyltoluidine.

Orthamidobenzylacetoparatoluidide, $NH_2\cdot C_6H_4\cdot CH_2\cdot NAc\cdot C_6H_4Me$, is obtained when pure nitrobenzylacetoparatoluidide is treated with zinc-dust and hydrochloric acid in cold alcoholic solution. It separates from alcohol in colourless crystals, melts at 99°, and is very readily soluble in cold benzene and warm alcohol, but more sparingly in light petroleum. When heated with concentrated hydrochloric acid at 100°, it is converted into orthamidobenzylparatoluidine (m. p. 80·5°).

Orthamidobenzylaniline, $NH_2\cdot C_6H_4\cdot CH_2\cdot NHPh$, can be prepared by heating orthonitrobenzyl chloride with aniline and reducing the product with zinc-dust and acetic acid; it crystallises from alcohol and benzene in colourless needles or prisms melting at 81—82°.

Orthamidobenzylbenzoylanilide, $NH_2\cdot C_6H_4\cdot CH_2\cdot NBzPh$, is obtained when orthonitrobenzylbenzoylanilide is reduced with zinc-dust and acetic acid. It crystallises from alcohol in short needles, melts at 115°, and is identical with the compound (m. p. 114·5°) described as phenylbenzylenebenzenylamidine by Lellmann and Stickel (*loc. cit.*). The *acetyl*-derivative, $C_{22}H_{20}N_2O_2$, prepared by boiling the base with

acetic anhydride, separates from warm alcohol, in which it is readily soluble, in colourless crystals melting at 164—165°. F. S. K.

Derivatives of Orthoparadinitrophenylphenylhydrazine. By C. WILLGERODT and B. HERMANN (*J. pr. Chem.* [2], **42**, 126—133). —The authors have determined the molecular weights of nitronitroso- and dinitroso-azobenzene by Raoult's method, and have thus confirmed their constitutions as derivatives of azobenzene (Abstr., 1889, 1160).

Paratrinitroazobenzene, $NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(NO_2)_2$ [$NO_2 : N = 4 : 1$, and $(NO_2)_2 : N = 4 : 2 : 1$], is obtained by mixing dinitrophenylphenylhydrazine or orthoparadinitroazobenzene with fuming nitric acid (sp. gr. 1·52), warming the mixture on the water-bath, and pouring it into cold water; it crystallises in red needles which melt at 170° (uncorr.), and dissolve in hot organic solvents, but not in water. With fuming nitric acid and chromic acid, it yields an oxidation-product, agreeing with Klinger and Zuurdeeg's paratrinitroazoxybenzene (this vol., p. 761), but it melts at 133°, not 136—137°; this confirms the constitution of this trinitroazobenzene.

Orthoparatetranitroazobenzene, obtained by further nitrating paratrinitroazobenzene, crystallises in beautiful orange tables, which melt at 222° (uncorr.), and are insoluble in water, sparingly soluble in alcohol and ether, and freely soluble in benzene, glacial acetic acid, and chloroform.

Trinitronitrosoazobenzene is prepared by heating nitronitrosoazobenzene with fuming nitric acid and adding water; it forms crystals which melt at 224° (uncorr.), and dissolve sparingly in hot water, hot alcohol, and ether, but freely in glacial acetic acid, benzene, and chloroform. Its constitution is uncertain.

Dinitrodinitrosoazobenzene is obtained by warming dinitrosoazobenzene [1 : 2 : 4] with fuming nitric acid for some time, and adding water. It crystallises in short, yellow needles which melt at 238°.

When dinitrophenylphenylhydrazine (2 grams) is dissolved in chloroform and acted on by bromine (0·63 gram), white needles melting at 242° are obtained on subsequent evaporation of the chloroform and crystallisation of the residue. The analysis of these crystals leaves the composition in doubt, save that the substance is a monobrominated derivative. When excess of bromine is used, crystals which melt at 190° are obtained; this also is of uncertain composition, but is certainly a dibrominated derivative; the same substance is produced by acting on dinitroazobenzene with excess of bromine, so it must almost certainly be a dinitrodibromazobenzene. A. G. B.

Derivatives of Diphenylhydrazine and Methylphenylhydrazine. By R. STAHEL (*Annalen*, **258**, 242—251).—Diphenylhydrazine, prepared by the method described by Fischer (*Annalen*, **190**, 179), and purified by distillation under reduced pressure, crystallises from light petroleum in well-defined, monoclinic plates, melts at 34·5°, and boils at about 220° (40 to 50 mm.). It combines only slowly with the ordinary sugars in alcoholic solution at the ordi-

nary temperature, but the reaction takes place more quickly on warming, sparingly soluble, crystalline hydrazones being formed.

Glucosediphenylhydrazone, $C_6H_{12}O_5{:}N_2Ph_2$, is prepared by boiling glucose with diphenylhydrazine in aqueous alcoholic solution for two hours; the alcohol is evaporated almost completely, ether added to precipitate the hydrazone, and the process repeated with the mother liquors; the yield is about 75 per cent. of the theoretical. It crystallises from hot water in small, colourless prisms, melts at 161—162°, and is readily soluble in hot water and alcohol, but almost insoluble in ether, benzene, and chloroform; it reduces Fehling's solution on boiling, and it is decomposed into its constituents by concentrated hydrochloric acid. The formation of this compound can be very conveniently employed for the detection of dextrose in presence of levulose.

Mannosediphenylhydrazone, $C_6H_{12}O_5{:}N_2Ph_2$, prepared in like manner, crystallises in small, colourless prisms, melts at 155°, and resembles the preceding compound in its properties.

Galactosediphenylhydrazone, $C_6H_{12}O_5{:}N_2Ph_2$, crystallises from hot water in colourless prisms, melts at 157°, and resembles the hydrazones described above in its behaviour with solvents.

Rhamnosediphenylhydrazone, $C_6H_{12}O_4{:}N_2Ph_2$, crystallises from hot water in colourless needles melting at 134°.

Furfuraldehyde diphenylhydrazone, $C_4H_3O{\cdot}CH{:}N_2Ph_2$, obtained by treating the aldehyde with the base, crystallises from dilute alcohol in yellowish needles, melts at 90°, and is readily soluble in alcohol and ether, but only sparingly in benzene, and insoluble in water; it dissolves in concentrated sulphuric acid, and in hydrochloric acid yielding a red solution, which turns dirty brown after a long time, whereas the solution in glacial acetic acid retains its red colour.

Salicylaldehyde diphenylhydrazone, $OH{\cdot}C_6H_4{\cdot}CH{:}N_2Ph_2$, prepared in like manner, crystallises from hot 80 per cent. alcohol in colourless needles, melts at 138·5°, and is readily soluble in ether and alcohol, but almost insoluble in water.

Diphenylthiocarbazinic acid, $NPh_2{\cdot}NH{\cdot}CS{\cdot}SH$, is deposited in well-defined golden prisms when a solution of diphenylhydrazine in carbon bisulphide is allowed to evaporate at the ordinary temperature; it melts at 109° with decomposition, is rather unstable, and is insoluble in water, but readily soluble in alcohol, ether, chloroform, and acetone. It dissolves unchanged in cold dilute soda, and in its alcoholic solution silver nitrate produces a yellow, mercuric chloride a violet-red, and ferric chloride a deep red precipitate. On distillation, it is decomposed into carbon bisulphide, hydrogen sulphide, and diphenylamine.

Dimethyldiphenylthiocarbazide, $CS(NH{\cdot}NPhMe)_2$, is obtained when methylphenylhydrazine is heated with carbon bisulphide for three hours at 100°. It separates from dilute alcohol in colourless crystals, melts at about 168° with decomposition, and is readily soluble in alcohol, but insoluble in water; it is not acted on by boiling dilute soda, bnt is completely decomposed by warm concentrated hydrochloric acid.

F. S. K.

Isomeric Oximes. By H. GOLDSCHMIDT (*Ber.*, **23**, 2163—2180; compare this vol., p. 251).—*Methylanisaldoxime*,

$$OMe\cdot C_6H_4\cdot CH\colon N\cdot OMe,$$

is obtained when anisaldoxime (m. p. 61°) is treated with sodium methoxide and methyl iodide in methyl alcoholic solution at the ordinary temperature. It crystallises from light petroleum in transparent, seemingly quadratic plates, melts at 43°, boils at 246° (724 mm.), and has a peculiar, agreeable odour; it is very readily soluble in alcohol, ether, and benzene, but more sparingly in light petroleum. No precipitate is produced when hydrogen chloride is passed into its alcoholic solution, whereas those alkyl-derivatives of aldoximes in which the alkyl is directly combined with nitrogen always give a precipitate, and, moreover, when heated with hydriodic acid it yields ammonia, but not methylamine; these reactions prove that the methyl-group is in direct combination with oxygen.

Isoanisilaldoxime, prepared by Beckmann's method (this vol., p. 1121), melts at 133°, and can be converted into the isomeride by heating it for a short time above its melting point.

Carbanilidoisoanisaldoxime, $OMe\cdot C_6H_4\cdot CH\colon N\cdot O\cdot CO\cdot NHPh$, is precipitated in yellowish plates, when phenylcarbimide is added to an ethereal solution of isoanisaldoxime. It melts at 80° with decomposition, and, like other carbanilido-derivatives of isoaldoximes, is very unstable; it decomposes spontaneously into diphenylcarbamide, anisonitrile, carbonic anhydride, and water, and when treated in benzene solution with a little hydrogen chloride it is converted into the much more stable isomeride melting at 82° (compare Goldschmidt, *loc. cit.*).

Methylisoanisaldoxime, $OMe\cdot C_6H_4\cdot CH\colon N\cdot OMe$, can be obtained in small quantities as follows:—Isoanisaldoxime is treated with the theoretical quantity of sodium ethoxide and then with an alcoholic solution of silver nitrate; the silver salt, which is precipitated in a colourless condition but rapidly darkens, is washed consecutively with alcohol and ether, treated with methyl iodide in cold ethereal solution, and after some hours the clear solution evaporated. It can also be obtained, together with another compound, which seems to be the methyl-derivative of the constitution $OMe\cdot C_6H_4\cdot CH{<}\begin{smallmatrix}O\\|\\NMe\end{smallmatrix}$, by treating anisaldoxime with sodium methoxide and methyl iodide; the two compounds are separated by distillation with steam. It is a colourless oil, distils unchanged at 245° when pure, and is volatile with steam. No precipitate is produced on passing hydrogen chloride into its ethereal solution. When kept for some hours with dilute hydrochloric acid, when treated with sodium hydrogen sulphite, or when boiled with a trace of iodine, it is converted into the solid isomeride (m. p. 43°).

Benzylanisaldoxime, prepared by treating anisaldoxime with sodium ethoxide and benzyl chloride, melts at 47° (compare Beckmann, *loc. cit.*); when warmed with hydriodic acid, it yields benzyl iodide, so that its constitution is expressed by the formula

$$OMe\cdot C_6H_4\cdot CH\colon N\cdot OC_7H_7.$$

Benzylisoanisaldoxime, melting at 106·5° (compare Beckmann, *loc. cit.*), gives benzylamine when heated with hydriodic acid; it has, therefore, the constitution $OMe{\cdot}C_6H_4{\cdot}CH{<}\genfrac{}{}{0pt}{}{O}{N{\cdot}C_7H_7}$.

Isometanitrobenzaldoxime, $NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OH$, can be prepared by passing hydrogen chloride into an ethereal solution of metanitrobenzaldoxime (m. p. 118—119°), and decomposing the hydrochloride obtained in this way with sodium carbonate. It crystallises from ether, in which it is only sparingly soluble, in colourless needles melting at 116—118°.

Carbanilidometanitrobenzaldoxime, $C_{14}H_{11}N_3O_4$, prepared by treating the oxime with phenylcarbimide in ethereal solution, crystallises from alcohol in yellowish needles, melts at 105°, and is readily soluble in alcohol and ether.

Carbanilidometanitroisobenzaldoxime, $C_{14}H_{11}N_3O_4$, prepared in like manner from the isoaldoxime, crystallises in small needles, melts at 75° with decomposition, and is only sparingly soluble in ether; it decomposes spontaneously, and when hydrogen chloride is passed into its ethereal solution, it is converted into the isomeride (m. p. 105°).

Methylmetanitroisobenzaldoxime, $NO_2{\cdot}C_6H_4{\cdot}CH{<}\genfrac{}{}{0pt}{}{O}{NMe}$, is formed together with small quantities of the isomeride (m. p. 69°) when metanitroisobenzaldoxime is treated with sodium methoxide and methyl iodide at the ordinary temperature; the whole is submitted to distillation with steam to separate the isomeride, the residue rendered alkaline, extracted with ether, and the ethereal solution evaporated. It crystallises in yellow prisms, melts at 117°, and is only moderately easily soluble in alcohol and ether; hydrogen chloride precipitates from its ethereal solution a colourless salt, and when heated with hydriodic acid it gives methylamine.

Methylmetanitroisobenzaldoxime, $NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}OMe$, can be obtained by treating the silver-derivative of the isoaldoxime, prepared by precipitating a solution of the sodium-derivative with silver nitrate, with methyl iodide in ethereal solution at the ordinary temperature. It crystallises from ether, alcohol, and benzene in almost colourless needles, melts at 69°, and is more sparingly soluble in ether and benzene than the isomeride (m. p. 63—63·5°) which has been previously prepared by Gabriel (*Ber.*, **15**, 3061); that the two compounds are not identical was proved by a crystallographic examination.

Benzylmetanitroisobenzaldoxime, $NO_2{\cdot}C_6H_4{\cdot}CH{<}\genfrac{}{}{0pt}{}{O}{N{\cdot}C_7H_7}$, prepared by treating the isoaldoxime with sodium ethoxide and benzyl chloride, crystallises from hot alcohol in yellow plates or needles, melts at 148°, and is sparingly soluble in cold ether and alcohol. It is decomposed by hydriodic acid with liberation of benzylamine, and when hydrogen chloride is passed into its ethereal solution a colourless precipitate is produced. The benzyl-derivative of metanitrobenzaldoxime was not obtained in a pure condition.

Methylcuminaldoxime, $C_6H_4Pr{\cdot}CH{:}N{\cdot}OMe$, prepared from cuminaldoxime (m. p. 58°), is a colourless liquid boiling at 245—246°

(705 mm.); the corresponding benzyl-derivative is a non-volatile oil.

Isocuminaldoxime, $C_{10}H_{13}NO$, crystallises from ether in small, colourless prisms, melts at 112°, and is more sparingly soluble in ether than cuminaldoxime. The *carbanilido*-derivative,

$$C_6H_4Pr\cdot CH\colon N\cdot O\cdot CO\cdot NHPh,$$

crystallises in small needles melting at 103° with decomposition.

The author's experiments show conclusively that both oximes and iso-oximes can form alkyl-derivatives of the constitution $X\cdot CH\colon N\cdot OR$; this fact proves that Beckmann's view of the isomerism of oximes is not correct. The author agrees with Hantzsch and Werner (this vol., p. 348), that the two forms are stereochemically isomeric, and have the constitution $\begin{array}{c}X\cdot CH\\ \| \\ RO\cdot N\end{array}$ and $\begin{array}{c}X\cdot CH\\ \| \\ N\cdot OR\end{array}$ respectively; since the carbanilido-derivatives of the iso-oximes are much more readily converted into nitriles than the corresponding derivatives of the normal oximes, the hydrogen-atom and the $CO\cdot NHPh$-group must be nearer together in the iso- than in the normal compounds; it follows, then, that carbanilido- and carbanilidoiso-benzaldoxime have the constitution

$$\begin{array}{r}Ph\cdot CH\\ \| \\ NHPh\cdot CO\cdot O\cdot N\end{array} \text{ and } \begin{array}{l}Ph\cdot CH\\ \| \\ N\cdot O\cdot CO\cdot NHPh\end{array}$$

respectively, and the aldoximes themselves are analogously constituted, a conclusion which is in accordance with Hantzsch and Werner's view.

Carbanilidoisobenzaldoxime is not converted into the isomeride by pure phenylcarbimide; the intramolecular change previously observed must therefore have been due to some impurity, probably hydrochloric acid. The intramolecular change observed by Beckmann (*loc. cit.*) which takes place when benzaldoxime is treated with phenylcarbimide, is probably due to the same cause.

That phenylcarbimide is a very suitable agent for determining the constitution of compounds such as the isomeric oximes, is proved by the above experiments, and V. Meyer's statement, that it is prone to bring about intramolecular change, is not correct. F. S. K.

Stereochemical Isomerism of Asymmetrical Monoximes. By A. HANTZSCH (*Ber.*, **23**, 2322—2325).—This isomerism is shown to be due to the asymmetry of the molecule. A list of compounds of the general formula $\begin{array}{c}X\cdot C\cdot Y\\ \| \\ RO\cdot N\end{array}$ and $\begin{array}{c}X\cdot C\cdot Y\\ \| \\ N\cdot OR'\end{array}$, which exhibit the isomerism is then given. In these X and Y are displaced by the groups C_6H_5, C_4H_3S (from thiophen), C_4H_3O (from furfuran), $C_6H_4Cl(p)$, $C_6H_4Me(p)$, $C_6H_4\cdot OMe(p)$, H, OH, CO, COOH, and CNOH. The displacement of X or Y by an alcoholic radical, such as methyl, appears to prevent the occurrence of stereochemical isomerism. C. F. B.

Isomeric Oximes of Unsymmetrical Ketones and the Configuration of Hydroxylamine. By K. AUWERS and V. MEYER (*Ber.*, **23**, 2403—2409).—The researches of the authors on the

oximes of bromo- and chloro-benzophenone (compare this vol., p. 1144), together with the recent investigations of Hantzsch and Werner on the oximes of unsymmetrical ketones, have shown that the isomerism of these compounds, and also of the benzil-oximes, cannot be explained by any assumption of structural dissimilarity. The real reason must therefore be sought, either in the nitrogen itself, or in the nature of the hydroxylamine-group. Hantzsch and Werner have advanced the former hypothesis, whilst the authors consider the latter to be the true explanation. Assuming the correctness of the theories of Van't Hoff and Wislicenus regarding the arrangement of atoms in space, the combined effect of the attraction of the nitrogen and oxygen on the hydroxylic hydrogen of hydroxylamine would cause it to be in a plane different from that occupied by the remaining atoms in the molecule. This hypothesis suffices to explain all observed facts; unsymmetrical oximes would therefore exist in two forms, $\overset{a}{\underset{b}{\mathrm{C}}}\!:\!\mathrm{N}\overset{\mathrm{H}}{\overset{|}{\mathrm{O}}}$ and $\overset{a}{\underset{b}{\mathrm{C}}}\!:\!\mathrm{N}\cdot\underset{\mathrm{H}}{\underset{|}{\mathrm{O}}}$. The difference between this theory and that of Hantzsch and Werner is shown by the two formulæ

$$\underset{(\mathrm{H.\,\&\,W.})}{\mathrm{C}{=}\overset{\mathrm{OH}}{\overset{|}{\mathrm{N}}}} \quad \text{and} \quad \underset{(\mathrm{A.\,\&.\,M.})}{\mathrm{C}{=}\mathrm{N}{-}\overset{\mathrm{H}}{\overset{|}{\mathrm{O}}}}.$$

The formation of oximes by the action of nitrous acid is readily accounted for on the ground of its being a substituted hydroxylamine; moreover, the fact that no case of geometrical isomerism has ever been observed in the azo-, azoxy-, and imido-compounds tells in favour of this theory. On the other hand, the authors point out that no optically active hydroxylamine-derivatives have yet been prepared, although their existence is indicated by this hypothesis; the same objection may, however, be urged against the theory of Hantzsch and Werner. J. B. T.

A Second Benzoïnoxime. By A. WERNER (*Ber.*, **23**, 2333—2336).—The benzoïnoxime hitherto known, melting at 151°, has always been prepared with the aid of heat. When, however, a solution of hydroxylamine hydrochloride (1 mol.) is added to benzoïn (1 mol.), in minute crystals, suspended in dilute alcohol, the mixture neutralised with sodium carbonate, a solution of sodium hydroxide (1 mol.) then added, and the whole allowed to remain for several days at the ordinary temperature, the benzoïn slowly dissolves, and if the mixture is now poured into water and the whole acidified with acetic acid, it turns milky, and a substance separates which after a day or two gradually solidifies to a mass of crystals; these, when washed with ether, dissolved in alcohol, and reprecipitated with water, yield a new *β-benzoïnoxime* in white needles melting at 95—99°. By Raoult's method it was shown that both this and the ordinary α-oxime have the formula $C_{14}H_{13}NO_2$. The new oxime is decomposed into benzoïn and hydroxylamine when heated with alcoholic hydrochloric acid, and it can be converted into the α-isomeride; this is best effected by boiling it with dilute alcohol containing a little alkali. C. F. B.

Amidoximes. By P. HOCHHEIM (*Inaugural Dissertation, Chem. Centr.*, 1890, i. 939).—*Anisylnitrile*, $C_7H_7O·CN$, prepared from copper cyanide and diazoanisyl hydrochloride solution, boils at 255—256°. *Anisylamidoxime*, $C_7H_7O·C(NOH)·NH_2$, melting point 122°, is prepared from the nitrile by the action of hydroxylamine. Its solution is coloured blood-red by ferric chloride; with Fehling's solution, it forms a dirty-green copper salt, and it reduces ammonia silver solution; the hydrochloride melts at 168°, the platinochloride at 196°, and the copper salt, $C_7H_7O·C(NO·Cu·OH)·NH_2$, at 212°.

Anisylazoximeethenyl, $C_7H_7O·C\lt\genfrac{}{}{0pt}{}{NO}{N}\gt CMe$, melting at 116°, is prepared from the amidoxime by the action of acetic anhydride or acetic chloride. With bromine, a monobrominated compound and a dibrom-additive compound are obtained, the former melting at 75° and the latter at 110°. With succinic anhydride, anisylamidoxime forms *anisylazoximepropenyl-ω-carboxylic acid*,

$$C_7H_7O·C\lt\genfrac{}{}{0pt}{}{NO}{N}\gt C·CH_2CH_2·COOH + H_2O,$$

which softens at 128°, and melts at 131°. The lead salt was analysed. *Chloralanisylamidoxime*, $C_7H_7O·C(NOH)(NH_2),C_2HCl_3O$, is prepared by heating its components together; it melts at 139°. *Anisylimidoximecarbonyl*, $C_7H_7O·C\lt\genfrac{}{}{0pt}{}{NO}{NH}\gt CO$, melting point 195°, is prepared from anisylamidoxime and ethyl chlorocarbonate. The corresponding *thio*-compound is prepared by heating the amidoxime with carbon bisulphide; it melts at 125—126°. *Anisyluramidoxime*, $C_7H_7O·C(NOH)·NH·CONH_2$, melting at 136° with decomposition, is prepared from anisylamidoxime hydrochloride and potassium cyanate. *Anisylphenyluramidoxime*, $C_7H_7O·C(NOH)·NH·CO·NHPh$, prepared by the action of phenyl isocyanate (carbanil), melts at 136°, and is converted by the action of acetic anhydride and sodium acetate into anisylazoximeethenyl, whilst glacial acetic acid converts it into diphenylcarbamide and anisylamidoxime. Phenyl thiocarbimide combines with anisylamidoxime, forming a compound of the formula $C_{15}H_{13}N_3SO$, which the author has provisionally named *anhydroanisylphenylthiouramidoxime.* With mercuric oxide, only diphenylthiocarbamide could be obtained from it; with nitric acid a dinitro-derivative, melting at 206°, is obtained. J. W. L.

Constitution of Eurhodine, Induline, and Allied Dyes. By F. KEHRMANN (*Ber.*, **23**, 2446—2454).—*Quinoneimides and Amidoquinones.*—On treating a dilute solution of the sodium-derivative of tetrahydroxyquinone with an orthophenyldiamine salt, and adding acetic acid, a compound separates in greenish-brown crystals; it is the analogue of the tolueneazine prepared by Nietzki and Kehrmann (compare Abstr., 1887, 473, and 1888, 262), and has the formula $C_6H_4\lt\genfrac{}{}{0pt}{}{N-}{NH-}\gt C_6(OH)_3O$ [N : NH·O = 2 : 3 : 5]. It is very sparingly soluble in organic solvents, and rapidly oxidises on exposure to air, forming dihydroxyquinonephenazine; it dissolves in dilute mineral

acids with a dark olive-green colour. By careful oxidation, the corresponding rhodizonic acid-derivative is obtained, insoluble in ammonia, but soluble in alkaline hydroxides with a violet-blue colour. Chloroparadihydroxyquinone reacts with orthophenylenediamine in a similar manner; after purification, the product crystallises from glacial acetic acid in concentric, garnet-red needles; it has the formula

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{N-}{NH}}{>}C_6HCl(OH)O\ [Cl : H : O : OH = 1 : 4 : 5 : 6],$$

and is a feeble acid, uniting with alkaline hydroxides and carbonates to form reddish-yellow, soluble salts. The compound also combines with acids, but the salts are very unstable, and are entirely dissociated on adding water. With concentrated sulphuric acid, a dirty-green colour is produced, which changes to reddish-brown on dilution. The *hydrochloride* crystallises in long, brownish-red needles. This compound is undoubtedly analogous to the dihydroxyphenazine prepared by O. Fischer and Hepp (compare this vol., p. 800). Dichloroparadihydroxyquinone, nitroparadihydroxyquinone, and certain allied hydroxyquinones do not condense with orthophenylenediamine, toluylenediamine, or naphthalenediamine, but simply combine to form the respective salts, which may be recrystallised without decomposition. α-Naphthenrhodol is prepared by warming sodium hydroxynaphthaquinone with an orthophenylenediamine salt, in presence of acetic acid; the product is purified by treatment with sodium hydroxide solution, and the salt decomposed with acetic acid; it crystallises from glacial acetic acid in needles, and is identical with the compound obtained by Fischer and Hepp (*loc. cit.*) from amido-1 : 2-naphthaphenazine; the formula should therefore be

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{-N}{NH}}{>}C_{10}H_5O,$$

instead of $C_6H_4{<}{\genfrac{}{}{0pt}{}{N}{N}}{>}C_{10}H_5\cdot OH$. α-Amidonaphthaphenazine is prepared by heating a concentrated alcoholic solution of hydroxynaphthaquinone and orthophenylenediamine hydrochloride in molecular proportion on the water-bath for 15 minutes. The solution becomes red, and solidifies to a mass of slender, red needles of the hydrochloride; the free base, $C_6H_4{<}{\genfrac{}{}{0pt}{}{-N}{NH}}{>}C_{10}H_5{:}NH$, is liberated by the action of ammonia; it has previously been obtained by Fischer and Hepp (*loc. cit.*) from benzeneazonaphthylamine and orthophenylenediamine. The formation of this compound proves definitely that, apart from possible tautomerism, hydroxynaphthaquinoneimide is represented by the formula $C_{10}H_5O(OH)(NH)$ [O : OH : NH = 1 : 2 : 4]. J. B. T.

Two Stereochemically Isomeric Derivatives of Furfuraldoxime. By A. Werner (*Ber.*, **23**, 2336—2339).—Furfuraldoxime was converted into its benzyl-derivative by the method of Japp and Klingemann. The product crystallised in small plates melting at 88°. When boiled with hydriodic acid, no benzyl iodide is formed, but when the mixture is heated at 180°, a small amount of benzylamine is obtained.

The formula of the benzyl-derivative is, therefore, $\mathrm{O}<\begin{matrix}\mathrm{CH\cdot C_4H_3O}\\ |\\ \mathrm{N\cdot CH_2Ph}\end{matrix}$. This is confirmed by its synthesis from furfuraldehyde and β-benzylhydroxylamine; the latter being prepared from the benzyl-derivative of isobenzaldoxime, melting at 110° (which was incidentally shown by Raoult's method to have a molecular weight corresponding with the formula $\mathrm{O}<\begin{matrix}\mathrm{CPh}\\ |\\ \mathrm{N\cdot CH_2Ph}\end{matrix}$), by neutralising it in aqueous solution with soda. When the above benzyl-derivative of furfuraldoxime is dissolved in ether, and hydrogen chloride passed in, and the hydrochloride thus formed is treated with soda, an isomeric benzyl-derivative is obtained, which crystallises from ether in long, shining needles melting at 65°. These, when allowed to remain, lose their transparency, and are converted into the isomeric modification melting at 88°. It is said to be a case of geometrical isomerism. C. F. B.

Oxazolines. By S. GABRIEL and T. HEYMANN (*Ber.*, 23, 2493—2502).—Bromethylbenzamide is rapidly dissolved in hot water, the equivalent quantity of sodium hydroxide immediately added, and the solution distilled in a current of steam; the distillate is extracted with ether, and on evaporation, *μ-phenyloxazoline*, $\begin{matrix}\mathrm{CH_2\cdot O}\\ |\\ \mathrm{CH_2\cdot N}\end{matrix}\!\!>\mathrm{CPh}$, is obtained; it is a colourless, strongly refractive liquid, boiling at 242—243°, and is miscible with alcohol, ether, and, to a less degree, with water. The yield is 50 per cent. of the theoretical. The same compound is also formed by the action of dilute aqueous sodium hydroxide, or alcoholic potash, on bromethylbenzamide.

The *picrate* is deposited in yellow needles melting at 177°. The *platinochloride* crystallises in orange-yellow needles. The *dichromate*, $(C_9H_9NO_2)_2,H_2Cr_2O_7$, forms yellowish-red needles; the *ferrocyanide* is precipitated as a yellowish-green, crystalline powder. On warming phenyloxazoline with excess of hydrobromic acid, bromethylbenzamide is regenerated; but if the *base* is in slight excess, and the solution is boiled for some time, *amidoethyl benzoate hydrobromide*, $\mathrm{OBz\cdot CH_2\cdot CH_2\cdot NH_2,HBr}$ (m. p. 142—143°), is produced; it is also obtained by boiling bromethylbenzamide with water; its constitution is shown by the formation of benzoylglycol by the action of potassium nitrite; this compound has been previously described (compare Abstr., 1889, 1134) as hydroxyethylbenzamide,

$$\mathrm{OH\cdot CH_2\cdot CH_2\cdot NHBz},$$

but the above results show this to be incorrect. With an equivalent quantity of hydrochloric acid, phenyloxazoline yields *β-amidoethylbenzoate hydrochloride*, crystallising from alcohol, on the addition of ethyl acetate, in flat needles which melt at 133—135°. With excess of hydrochloric acid, the oxazoline yields, *β-chlorethylbenzamide*, $\mathrm{CH_2Cl\cdot CH_2\cdot NHBz}$, crystallising from light petroleum or water in needles melting at 102°.

$\beta\mu$-Methylphenyloxazoline, $\begin{matrix}\mathrm{CHMe\cdot O}\\ |\\ \mathrm{CH_2 - N}\end{matrix}\!\!>\mathrm{CPh}$, is obtained from

β-bromopropylbenzamide by methods similar to those employed for the preparation of phenyloxazoline, and also by the action of alcoholic potassium hydrosulphide; it is a clear, colourless liquid, boiling at 243—244° under a pressure of 750 mm. The *platinochloride* is orange-yellow; the *picrate* melts at 167°; the *chromate* is precipitated as an oil which quickly crystallises; the *ferrocyanide* forms a greenish-yellow, crystalline powder. With excess of hydrobromic acid, the oxazoline is reconverted into β-bromopropylbenzamide. With excess of hydrochloric acid, *β-chloropropylbenzamide*,

$$CHMeCl\cdot CH_2\cdot NHBz,$$

is formed, crystallizing from light petroleum in small needles, melting at 72—73°. *β-amidopropyl benzoate hydrobromide*,

$$NH_2\cdot CH_2\cdot CHMe\cdot OBz,HBr,$$

is prepared by boiling an aqueous solution of β-bromopropylbenzamide, or a mixture of the oxazoline hydrobromic acid in molecular proportion; it crystallises from glacial acetic acid in colourless needles melting at 132—133°. On heating this compound with potassium hydroxide, β-hydroxypropylbenzamide (m. p. 92—93°) is formed. No corresponding reaction of amidoethyl benzoate was observed. With potassium nitrite, benzoylpropylene glycol is obtained. The free *base* is prepared by adding an alkali to the hydrobromide: it is a colourless, viscid liquid, readily miscible with water. The *picrate* crystallises in flat needles melting at 188—189°. The *platinochloride* is deposited from hot water in flat yellowish needles. μ-Methyloxazoline picrate has previously been prepared (*loc. cit.*), the yield is slightly larger if bromethylamine hydrobromide is boiled for 15 minutes with an equal weight of acetic anhydride, and treated with a solution of sodium picrate. The product obtained on boiling this compound with water is the picrate of *amidoethyl acetate*, $NH_2\cdot CH_2\cdot CH_2\cdot OAc$, not hydroxyethylacetamide as previously stated.

J. B. T.

Tetraphenyltetracarbazone. By J. CULMANN (*Annalen*, **258**, 235—242).—The compound (m. p. 137°) prepared by Hess (Abstr., 1886, 547) by treating bromacetophenone with phenylhydrazine has the molecular formula $C_{28}H_{24}N_4$, as is proved by molecular weight determinations in benzene solution; the experiments described below show that it has most probably the constitution $\begin{matrix} CH_2\cdot CPh{:}N\cdot NPh \\ | \qquad\qquad\quad | \\ CH_2\cdot CPh{:}N\cdot NPh \end{matrix}$ and it is named *tetraphenyltetracarbazone* by the author, the term *tetracarbazone* being applied to the ring $C_4H_4N_4$.

When tetraphenyltetracarbazone (1 part) is dissolved in a saturated ice-cold alcoholic solution (5 parts) of hydrogen chloride, it is converted into a compound of the composition $C_{22}H_{18}N_2$, aniline, and small quantities of a base of the composition, $C_{22}H_{17}N_3$. After keeping for 10 minutes, the solution is poured into ice-cold water, the precipitate separated by filtration, washed with cold alcohol to free it from resinous products, and the residue crystallised from hot alcohol.

The compound of the composition $C_{22}H_{18}N_2$ separates from the alcoholic solution, on cooling, in yellow needles, melts at 116°, and decomposes at a higher temperature; it is insoluble in water, but moderately easily soluble in hot alcohol and glacial acetic acid. It is probably the phenylhydrazine-derivative of diphenacyl, as, on oxidation with potassium dichromate and sulphuric acid, it yields a large quantity of benzoic acid, and when warmed with 30 per cent. sulphuric acid it is decomposed into dibenzoylethane (phenacylacetophenone), identical with the compound (m. p. 144°) obtained by Claus and Werner (Abstr., 1887, 827) and named diphenacyl by Kraft and Paal (Abstr., 1889, 147); a substance, melting at 229°, the composition of which was not determined, is also formed in very small quantities in this decomposition.

The base of the composition $C_{22}H_{17}N_3$ is gradually deposited from the acid alcoholic mother liquors obtained in the decomposition of tetraphenyltetracarbazone, in the form of the *hydrochloride*,

$$C_{22}H_{17}N_3,HCl.$$

This salt crystallises from hot dilute hydrochloric acid in colourless, slender needles, melts above 300°, and is moderately easily soluble in hot alcohol and water. The *nitrate* crystallises in plates. The free *base* is an orange-yellow, amorphous compound, and has perhaps the constitution $\begin{matrix} CH{\cdot}CPh{:}N \\ \| \\ CH{\cdot}CPh{:}N \end{matrix}\!\!>\!NPh.$

All attempts to prepare the two decomposition-products of tetraphenyltetracarbazone synthetically from diphenacyl, or its dihydrazone, were unsuccessful. F. S. K.

Thiophenylmethylpyrazolone. By A. MICHAELIS (*Ber.*, **23**, 2476—2478).—The compound obtained by the action of phenylhydrazine on ethyl thioacetoacetate (compare this vol., p. 582) has the formula $C_{20}H_{18}O_2N_4S$, instead of $C_{20}H_{22}O_4N_4S$ as stated, and is identical with the thiophenylmethylpyrazolone described by Buchka and Sprague (compare this vol., p. 796). J. B. T.

Aromatic Mercury Compounds. By A. MICHAELIS and J. RABINERSON (*Ber.*, **23**, 2342—2346).—*Mercurodimethylaniline chloride*, $HgCl{\cdot}C_6H_4{\cdot}NMe_2$, is prepared by mixing alcoholic solutions of mercuric chloride and mercurodimethylaniline; the compound is immediately deposited in white, lustrous plates melting at 225° with decomposition; it is soluble in chloroform, and in cold dilute hydrochloric acid, from which it is precipitated unchanged by sodium carbonate; it is decomposed into its components on warming with dilute acid. The same compound may be obtained by treating a benzene solution of mercurodimethylaniline with hydrochloric acid. *Mercurodimethylaniline bromide*, $HgBr{\cdot}C_6H_4{\cdot}NMe_2$, is prepared in a manner similar to the chloride, and melts at 226°. The *iodide*, $HgI{\cdot}C_6H_4{\cdot}NMe_2$, crystallises in colourless plates melting at 195°.

Paramercurodianisoïl, $Hg(C_6H_4{\cdot}OMe)_2$, prepared from parabromanisoïl, crystallises from benzene in slender, white needles melting at 202°, is readily soluble in chloroform, and sublimes when carefully

heated; the yield is about 40 per cent. *Mercuranisoïl chloride*, $HgCl\cdot C_6H_4\cdot OMe$, is obtained in the same manner as the dimethylaniline-derivative; it crystallises in colourless, lustrous plates melting at 239°. The corresponding *bromide*, $HgBr\cdot C_6H_4\cdot OMe$, melts at 187°; and the *iodide*, $HgI\cdot C_6H_4\cdot OMe$, at 227°. *Mercuranisoïl acetate*, $OAc\cdot Hg\cdot C_6H_4\cdot OMe$, is formed by treating mercurodianisoïl with glacial acetic acid; it crystallises from alcohol in needles melting at 176·5°. *Mercuranisoïl oxide* $O(Hg\cdot C_6H_4\cdot OMe)_2$, is prepared by warming any one of the above haloïd compounds with sodium carbonate solution; the white powder which is obtained on cooling is washed with water, and recrystallised from alcohol; it is deposited in small, white, slender needles melting at 177°; it is very sparingly soluble in water, but dissolves readily in warm sodium carbonate solution. The aqueous solution has an alkaline reaction, but it does not combine with carbonic anhydride on exposure to the air.

J. B. T.

A Product of the Condensation of Ethyl Cyanacetate and Benzaldehyde. By J. T. CARRICK (*J. pr. Chem.* [2], **42**, 159—160).—In the presence of sodium ethoxide (0·2 gram of sodium), benzaldehyde (5 grams) and ethyl cyanacetate (5 grams) readily undergo condensation, brilliant crystals of the empirical composition $C_{12}H_{11}NO_2$ separating out. An oily product is also formed, but it has not been investigated.

The condensation-product is decomposed with difficulty by strong sulphuric or nitric acid; when heated with strong hydrochloric acid at 150°, it yields benzaldehyde and carbonic anhydride. Aqueous alkalis decompose it in the cold with formation of benzaldehyde. Alcoholic methylamine forms with it a compound, $(C_{20}H_{12}N_2O_2)_2NMe$; alcoholic ammonia has a similar action; aqueous ammonia dissolves it, and acids precipitate a nitrogenous substance from the solution.

A. G. B.

Vanillin from Rosa canina. By SCHNEEGANS (*J. Pharm.* [5], **22**, 115; from *J. Pharm. Elsass-Loth.*, 1890, 97).—The powdered seeds are extracted by means of ether; part of the ether is separated by distillation, and the residue is agitated with hydrogen sodium sulphite solution saturated with sulphurous anhydride. To the aqueous solution, treated repeatedly with ether to remove fatty compounds, is next added excess of dilute sulphuric acid; the sulphurous anhydride set free is removed by a current of air, and ether is again added to extract a brown oil which, after some days, becomes a mass of crystals. These crystals, decolorised by charcoal, give the characteristic reactions of vanillin; the yield is exceedingly small, only about 1 in 10,000. J. T.

Constitution of Quinone. By J. U. NEF (*J. pr. Chem.* [2], **42**, 161—188).—It has been shown by Stenhouse (this Journ., 1870, p. 8) that chloranilic acid is readily converted into the ethyl salt, $C_6Cl_2O_2(OEt)_2$, by treating silver chloranilate with ethyl iodide. This compound has all the properties of a quinone, and must contain the ethyl-groups combined with the oxygen, as otherwise its constitution would

be represented by the formula $\frac{Et}{Cl}\!>\!C\!<\!\frac{CO\cdot CO}{CO\cdot CO}\!>\!C\!<\!\frac{Et}{Cl}$, in which case it must, on reduction, take up four atoms of hydrogen. Experiment has, however, shown that, under these circumstances, two, and only two, atoms of hydrogen can be taken up, the compound formed being *ethyl hydrochloranilate*, $C_6Cl_2(OH)_2(OEt)_2$, which has previously been prepared by Kehrmann (this vol., p. 136). It is not attacked by sodium amalgam, even when digested with it for six hours on the water-bath, and is converted on boiling with acetic anhydride into the diacetyl-compound, $C_6Cl_2(OAc)_2(OEt)_2$, which crystallises from alcohol in colourless, four-sided prisms melting at 172°, and volatilising without decomposition.

Diacetylchloranilic acid, $C_6Cl_2O_2(OAc)_2$, is readily obtained by adding an ethereal solution of acetic chloride to silver chloranilate suspended in ether free from alcohol and water. It crystallises from ether or anhydrous benzene in yellow needles, melts at 182·5°, and distils unchanged. Its alcoholic solution speedily undergoes decomposition in presence of traces of water.

These results show conclusively that chloranilic acid contains two hydroxyl-groups. It is, however, somewhat surprising that the hydrogen-atoms cannot be removed by oxidation, and it would appear possible that the two pairs of hydroxyl-groups in hydrochloranilic acid have a different value. If such were the case, we should then get two different paradichlorodimethoxydiethoxybenzenes by the ethylation of dimethyl hydrochloranilate, and by the methylation of diethyl hydrochloranilate respectively, whereas it is found that one and the same compound is obtained in both cases. This crystallises in long, colourless needles which melt at 103°, and are very soluble in organic solvents. On oxidation, it gives a mixture of methyl and ethyl chloranilates.

By the action of bromine in dry carbon bisulphide solution on silver chloranilate, *dibromodichlorotetraketohexamethylene* is formed, the following reaction taking place:—

$$ClC\!<\!\frac{CO\cdot C(OAg)}{C(OAg)\cdot CO}\!>\!CCl + 2Br_2 = \frac{Cl}{Br}\!>\!C\!<\!\frac{CO\cdot CO}{CO\cdot CO}\!>\!C\!<\!\frac{Cl}{Br} + 2AgBr.$$

That the bromine does not simply take the place of the silver with formation of a bromoxyl-derivative is proved by the fact that the same compound is obtained by the action of chlorine on silver bromanilate. Dibromodichlorotetraketohexamethylene crystallises in pale-yellow, flat, hygroscopic needles, which when heated quickly in small quantities sublime unchanged, but commence to decompose at 110° when slowly heated. Its solution in carbon bisulphide has a slight green fluorescence. It does not give characteristic compounds with phenylhydrazine or orthodiamidotoluene, and is very readily decomposed by water, with evolution of carbonic anhydride and formation of pentamethylene-derivatives. On reduction with sulphurous acid, it is reconverted into chloranilic acid.

Tetrachlorotetraketohexamethylene, $Cl_2C\!<\!\frac{CO\cdot CO}{CO\cdot CO}\!>\!CCl_2$, is obtained in a similar manner by the action of chlorine on silver chloranilate,

and crystallises in long, pale-yellow needles, which are not reduced to chloranilic acid by the action of sulphurous acid. The chlorine-atoms are therefore more firmly combined than the bromine-atoms.

Tetrabromotetraketohexamethylene, $Br_2C<\begin{matrix}CO\cdot CO\\CO\cdot CO\end{matrix}>CBr_2$. To prepare this compound, silver bromanilate is treated with bromine in the manner already described. It crystallises in flat, pale-yellow needles, which cannot be sublimed without decomposition, even when quickly heated. When water is poured on to it, a vigorous effervescence takes place, carbonic anhydride being evolved, and a compound having the composition $C_5Br_3O_3H$ remaining in solution, which is identical with the compound described by Hantzsch as tribromotriketopentamethylene (Abstr., 1888, 1190). It behaves, however, as a monobasic acid, and the author therefore regards it as *tribromhydroxydiketodihydropentene*, $\begin{matrix}CO\cdot CBr\\|\\CO\cdot CBr_2\end{matrix}>C\cdot OH$. He further believes that tetrabromotetraketohexamethylene is always the first intermediate product in the formation of pentamethylene-derivatives from the anilic acids; that it has not previously been isolated is due to the fact that the reaction has been carried out in aqueous solution, in which this compound is immediately decomposed. A tetrabromotetraketohexamethylene has indeed been described by Hantzsch, but according to the author, this is a mixture of tribromohydroxydiketodihydropentene and unaltered bromanilic acid.

Tetrachlorotetraketohexamethylene is also decomposed by water, forming the corresponding trichlorhydroxydiketodihydropentene. As an intermediate product, tetrachlorhydroxydiketopentamethylenecarboxylic acid is probably formed, but could not be isolated; the author doubts, therefore, whether the stable compound described by Hantzsch under that name (this vol., p. 131) has, in reality, the constitution assigned to it.

These results show that there is no necessity for assuming tautomerism in the chloranilic acids, as in its salts the metal is in no case directly combined with a carbon-atom.

When quinone is treated with 1 mol. of bromine in chloroform solution, it is converted into *quinone dibromide*, $C_6H_4O_2Br_2$. This crystallises in flat, yellow needles, which have a greenish surface lustre, and melt at 86°. It has a slight quinone-like odour, and is converted by boiling water into monobromoquinone, and on treatment with zinc-dust and acetic acid, again forms quinone. This compound was obtained nine years ago by Sarauw (Abstr., 1881, 1135), who, however, on account of its somewhat peculiar behaviour, regarded it as an isomeric dibromoquinol.

If to a chloroform solution of quinone, 2 mols. of bromine be added, *quinone tetrabromide*, $C_6H_4O_2Br_4$, is obtained. This is a colourless and odourless compound, which is very sparingly soluble in all ordinary solvents, becomes yellow at 110°, and evolves hydrogen bromide rapidly at 170—175°. On boiling with aqueous alcohol, it is converted into a mixture of equal parts of meta- and para-dibromoquinone. On reduction with zinc-dust and acetic acid, it is also reconverted into quinone.

The formation of a dibromide and tetrabromide follows naturally from Fittig's formula for quinone, $CO<\begin{smallmatrix}CH{:}CH\\CH{:}CH\end{smallmatrix}>CO$, but not from the peroxide formula. Their formation can also be explained by Claus' diagonal formula, $CO<\begin{smallmatrix}CH\cdot CH\\ \times \\CH\cdot CH\end{smallmatrix}>CO$, but if this were correct, the anilic acids, such as chloranilic acid, the formula of which would then be $<\begin{smallmatrix}CCl\cdot(OH)C\\ \times \\C(OH)\cdot ClC\end{smallmatrix}>CO$, should readily pass into derivatives of diquinoyl, $CO<\begin{smallmatrix}\text{---}CCl\cdot CO\\ \vert \\CO\cdot Cl\text{---}\end{smallmatrix}>CO$, whereas, all attempts to effect this change have been without success.

H. G. C.

Stereochemically Isomeric Oximes of Paratolyl Phenyl Ketone. By A. HANTZSCH (*Ber.*, 23, 2325—2332).—Auwers (this vol., p. 503) was able to obtain but one oxime of paratolyl phenyl ketone, $OH\cdot N{:}CPh\cdot C_6H_4Me$. The author finds that the product obtained by his methods is in each case a mixture of two isomeric oximes which can be isolated by dissolving the mixture in acetic acid, and fractionally precipitating them by the careful addition of water. That which comes down first melts at 154°, and is termed the α-variety. The β-isomeride melts at 115—116°, and is much more soluble in all solvents except water. Raoult's method shows that both have the formula $C_{14}H_{13}NO$, so that this is a case of true isomerism, and not of polymerism. The β- cannot be converted into the α-variety, but it is remarkable that the α-variety is converted into the β- (of lower melting point) when it is heated at 140° with hydroxylamine hydrochloride in alcohol and water. When treated with benzyl chloride and sodium ethoxide in alcoholic solution, the two varieties behave differently. The α-oxime yields a benzyl-derivative, $C_6H_4Me\cdot CPh{:}N\cdot O\cdot CH_2Ph$, crystallising from alcohol in well-formed, long, brilliant prisms, which melt at 85°, and dissolve very easily in ether and very sparingly in alcohol. The β-oxime yields, although less easily, a stereochemical isomeride, which separates from alcohol as an oil that very slowly solidifies in spherical aggregates of small needles. It melts at 45—47°, and is only sparingly soluble in alcohol. It is easily convertible into the α-isomeride melting at 85°; for example, by dissolving it in ether and passing hydrogen chloride into the solution.

We have thus two series of derivatives of stereochemically isomeric paratolyl phenyl ketones: $\begin{matrix}Ph\cdot C\cdot C_6H_4Me\\ \Vert \\ N\cdot OH\end{matrix}$ and $\begin{matrix}Ph\cdot C\cdot C_6H_4Me\\ \Vert \\ HO\cdot N\end{matrix}$, with the following melting points:—

	Oximes.	Benzyl-derivative of oximes.
α	154°	85°
β	115—116°	45—47°

C. F. B.

Formation of Racemic Acid by the Oxidation of Unsaturated Acids. By O. DOEBNER (*Ber.*, **23**, 2372—2377; compare this vol., pp. 176, 1007).—The author has previously prepared 2′ : 4′-dicarboxylic acids of the quinoline series by the oxidation of 2′ : 4′-cinnamenylquinolinecarboxylic acids; the disruption of the molecule takes place at the position of the double bond in the cinnamenyl-group, $C_6H_5{\cdot}CH{:}CH$. If this reaction were a general one, certain other unsaturated acids containing the same group should yield fumaric or maleïc acids, which, in the presence of potassium permanganate, would be converted into racemic and mesotartaric acids respectively.

Cinnamenylacrylic acid, CHPh:CH·CH:CH·COOH (10 grams), is neutralised with potassium hydroxide, and the solution, diluted to 2 litres, is cooled to 2—3°, and a solution of potassium permanganate (15 grams) in water (2 litres) at the same temperature is gradually added; the solution smells strongly of benzaldehyde; it is allowed to remain for two or three hours, and is then filtered, and concentrated to about one-sixteenth its bulk; on adding hydrochloric acid to the solution, a considerable evolution of carbonic anhydride takes place, and benzoic acid is precipitated; this is separated, and the filtrate treated with excess of ammonia and calcium chloride. The insoluble mixture of calcium salts thus obtained is now dissolved in hydrochloric acid, diluted, boiled, and treated, first with excess of ammonia, and then with excess of acetic acid, the solution is quickly filtered, and on cooling calcium racemate crystallises out; from this the free acid and various other salts were prepared. No trace of mesotartaric acid could be detected. Piperic acid, oxidised in the same manner, yields piperonal and piperonylic acid, together with carbonic anhydride, racemic and oxalic acids. This result is an additional proof of the correctness of the formula

$$CH_2{<}^{O}_{O}{>}C_6H_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}COOH,$$

for piperic acid. Acetaldehyde, carbonic anhydride, oxalic and racemic acids are obtained from sorbic acid, which should, therefore, probably be represented by the formula CHMe:CH·CH:CH·COOH.

No fumaric acid was observed in any of these experiments, so that the question of its formation as an intermediate product remains an open one.

J. B. T.

Stereochemically Isomeric Oximes of Phenyl Thienyl Ketone and Phenylglyoxylic Acid. By A. HANTZSCH (*Ber.*, **23**, 2332—2333).—Phenyl thienyl ketoxime, $OH{\cdot}N{:}CPh{\cdot}C_4H_3S$, exists in two isomeric modifications, a more soluble, melting at 91—92°, and a less soluble, melting at 113—114°.

The oxime of phenylglyoxylic acid, OH·N:CPh·COOH, exists in a less soluble stable form, melting at 145°, and in a more soluble unstable form, melting at 125°, which can be converted directly into the other variety.

C. F. B.

Gallic Acid, Tannin, and Oak-tannin. By C. Böttinger (*Annalen*, **258**, 252—260).—When sodium is gradually added to an alcoholic solution of anhydrous gallic acid, a blue colour is produced where the metal comes in contact with the liquid, but the colour soon disappears again, and a basic salt of gallic acid is deposited. An alcoholic solution of tannin, under the same conditions, gives first a greenish-blue coloration and then a yellowish precipitate, the tannin being converted into gallic acid.

When sodium is added to a boiling amyl alcoholic solution of anhydrous tannin, the portions of the liquid in contact with the metal are coloured greenish-blue, and then a yellowish precipitate is produced, part of the tannin being converted into an amyl-derivative and part of it decomposed into gallic acid.

The acetyl-derivative of oak-tannin under the same conditions is decomposed into acetic acid, oak-tannin, and the amyl-derivative of the last-named compound. In ethyl acetate solution, tannin and tannin-derivatives of this ethereal salt are formed, together with small quantities of gallic acid. F. S. K.

Constitution of Benzene. Reduction-products of Phthalic Acid. By A. v. Baeyer (*Annalen*, **258**, 145—219; compare this vol., pp. 875 and 1130, and Abstr., 1889, 1176).—Phthalic acid, on reduction with sodium amalgam, gives various hydrophthalic acids which, just as is the case with the hydroterephthalic acids, behave like unsaturated compounds of the fatty series; the theory of both classes of compounds must, therefore, be based on the same principles.

As the author has recently (*Ber.*, **23**, 1272) had an opportunity of stating his present views, the constitution of benzene is not discussed in this paper, except in so far that he replies to the criticisms of Ladenburg (this vol., p. 881), and gives an explanation, omitted from the address delivered at the Kekulé festival, of the changes which take place in the process of substitution.

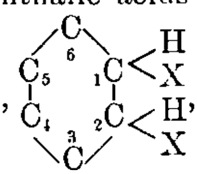
According to Kekulé, the formation of a substitution-product, such as bromobenzene, is preceded by the formation of an additive compound (benzene dibromide), from which the final product is formed by the elimination of hydrogen bromide, the double linking being at the same time regenerated. Since the simultaneous formation of both an ortho- and a para-compound in processes of this nature could not be explained in accordance with Kekulé's benzene formula, which, moreover, did not account for the complete symmetry (formation of only one ortho-compound) of the true benzene-derivatives, other formulæ, namely, those of Claus and Armstrong, were suggested: formulæ which would explain all substitution phenomena.

Kekulé's view has, however, now been proved to be correct experimentally; terephthalic acid, on reduction, yields a paradihydro-additive product, $\Delta^{2:5}$ dihydroterephthalic acid, the ethyl salt of which is reconverted into ethyl terephthalate on exposure to the air (compare Baeyer and Herb, this vol., p. 1130). The recent study of the behaviour of muconic acid on reduction (compare Baeyer and Rupe, *ibid.*, p. 875) has also shown that Kekulé's formula, which

before this time afforded an explanation of the formation of ortho-additive products only, can now account for the formation of para-additive compounds, and, consequently, also of para-eliminations.

After replying to some remarks of Claus (Abstr., 1889, 1061), and elaborating at some length the theory of the hydroterephthalic acids, the author proceeds to discuss the constitution of the hydrophthalic acids described below.

It will be proved beyond all doubt that the hexahydrophthalic acids contain the two carboxyl-groups in the ortho-position; this must, therefore, also be true as regards the tetra- and di-hydro-acids, which bear the same relation to the hexahydro-compounds as an unsaturated does to a saturated fatty acid.

According to the theory advanced in the case of the hydroterephthalic acids there may exist, exclusive of enantiomorphous forms, 11 position-isomeric and 4 geometrically isomeric hydrophthalic acids; 7 of these isomerides, namely, 1 dihydro-, 4 tetrahydro-, and 2 hexahydro-acids have already been prepared. The system of nomenclature employed for these compounds is the same as that used for the hydroterephthalic acids (Abstr., 1889, 1176), the formula of the hexahydro-acid,  numbered as shown, being the one to which all the others refer.

The only dihydrophthalic acid yet known resembles the dihydroterephthalic acids in its behaviour with reagents, and is probably the $\Delta^{2:4}$ acid, but until the other isomerides have been prepared its constitution must remain undecided.

The acid described below as Δ^2 tetrahydrophthalic acid has a constitution analogous to that of Δ^1 tetrahydroterephthalic acid, which it resembles in many respects, especially in being stable towards boiling soda.

The constitution of the acids described as Δ^1, Δ^4, and Δ^3 tetrahydrophthalic acid respectively is discussed below; it may, however, be here remarked that the conversion of the Δ^1 into the Δ^2 acid by hot potash is a change analogous to the conversion of citraconic into itaconic acid by boiling water, as may be seen by studying the constitutional formulæ of the four compounds. A comparison of their properties and behaviour shows the relationship between the Δ^1 acid and citraconic acid on the one hand, and the Δ^2 acid and itaconic acid on the other, still more plainly, and affords further evidence that the double binding in the aromatic acids is really in the Δ^1 and Δ^2 position respectively.

On comparing the properties of the hexahydrophthalic acids described below with those of the hexahydroterephthalic acids, it will be seen that in both cases the more sparingly soluble and higher-melting compound is stable towards hydrochloric acid, whereas the more readily soluble and lower-melting acid undergoes intramolecular change into the other form when treated with the halogen acid; this is also true in the case of hexahydro- and isohexahydro-

mellitic acids. The more readily soluble modification of hexahydroterephthalic acid has been previously compared with maleïc acid, and the more sparingly soluble with fumaric acid, but no proof has yet been given that the two carboxy-groups in the unstable form are really situated on the same side of the ring; that this is so as regards the unstable form of hexahydrophthalic acid can, however, be shown, but it is necessary first to prove that the two carboxy-groups are in the ortho-position.

The proof that the carboxy-groups of hexahydrophthalic acid are in the ortho-position is afforded by the fact that the acid is obtained by reducing the Δ^1 tetrahydro-acid, which from its resemblance to dimethylmaleïc acid (pyrocinchonic acid) and methylmaleïc acid (citraconic acid), and from its giving adipic acid on oxidation, must contain ortho-carboxyl-groups. Further, since only one hexahydrophthalic acid yields an anhydride (hexahydroisophthalic acid and hexahydroterephthalic acid do not), this particular one must contain the two carboxy-groups in the ortho-position; the complete analogy in the behaviour of hexahydrophthalic acid and dimethylsuccinic acid also shows that the former is an ortho-derivative.

The fact that the carboxyl-groups in hexahydrophthalic acid are in the ortho-position is a new proof of the incorrectness of the prism formula, in accordance with which they should be in the meta- or para-position.

Now, if the constitution of the two hexahydrophthalic acids is studied with the aid of Kekulé's atom-models, it will be seen that in one case the two carboxyl-groups are on the same side (maleïnoïd form), in the other on different sides (fumaroïd form) of the ring. Assuming that the readily soluble unstable acid is represented by the maleïnoïd formula, it should give an anhydride more readily than the isomeride; experiment has shown that this is the case. According to Wislicenus' hypothesis, the fumaroïd acid should not form an anhydride, but, as it does so, it must follow that, owing to greater "spannung," this anhydride will be less stable than that of the maleïnoïd acid, as will be seen by studying the molecule-models of the two compounds; this conclusion is also in accordance with observed facts, as, on heating, the fumaroïd is converted into the maleïnoïd form.

These arguments show that the more sparingly soluble hexahydrophthalic acid is the fumaroïd, and the readily soluble acid the maleïnoïd modification.

The explanation of the difference in behaviour between fumaric acid and the fumaroïd hexahydrophthalic acid, as regards anhydride formation, is given by an examination of the molecule-models of the two compounds.

According to Van't Hoff's theory, hexahydrophthalic acid may exist in an active and in an inactive modification, as it contains two asymmetric carbon-atoms; a consideration of the constitutional formulæ of the two acids will show that the maleïnoïd is the optically inactive modification, whilst the fumaroïd acid, although actually inactive is, just like racemic acid, composed of two active modifications, which, however, have not yet been separated from one another.

Dihydrophthalic acid cannot be obtained by the method previously described by Baeyer (Abstr., 1887, 370), as a mixture of isomeric tetrahydro-acids and a variable quantity of a hexahydro-acid is formed under these conditions. On reducing phthalic acid with sodium amalgam in cold sodium carbonate solution exactly as described by Graebe and Born (*Annalen*, **142**, 330), a mixture of dihydro- and tetrahydro-acids is produced; when phthalic acid is suspended in water, and treated with sodium amalgam, it is very quickly reduced, but phthalide and other compounds are formed.

Dihydrophthalic acid, $C_8H_8O_4$, can, however, be prepared by dissolving phthalic anhydride (60 grams) and crystalline sodium carbonate (120 grams) in water (420 grams) at the ordinary temperature, and adding 3 per cent. sodium amalgam (250 grams); as soon as the whole of the amalgam is decomposed, the solution is saturated with carbonic anhydride, and a further quantity (250 grams) of amalgam added, the process being repeated until 1500 grams have been employed. In about five days' time reduction is complete, the reaction being at an end when the lead salt of the acid obtained is readily soluble in 50 per cent. acetic acid. The decanted solution is slightly acidified with dilute hydrochloric acid, filtered, mixed with excess of dilute sulphuric acid, the precipitated acid separated by filtration, and recrystallised from hot water; the yield of the pure product is about 85 per cent. of the anhydride employed. It separates from water in well-defined, asymmetric crystals, melts at 215° when quickly heated, and is readily soluble (1 in 16) in boiling, but only sparingly (1 in 208) in cold water; its solution in sodium carbonate quickly decolorises potassium permanganate. The normal alkaline salts cannot easily be obtained, as, when a neutral solution is evaporated over sulphuric acid, crystals of the acid salt are deposited; the *potassium hydrogen* salt and the *sodium hydrogen* salt crystallise in plates. The *barium* salt is more readily soluble in hot than in cold water; the *barium hydrogen* salt crystallises in plates, and is more sparingly soluble than the normal salt. The *calcium* salt crystallises in needles, and is sparingly soluble, the *calcium hydrogen* salt in colourless plates, and is readily soluble in water. The *methyl* salt, $C_6H_6(COOMe)_2$, prepared by passing hydrogen chloride into a methyl alcoholic solution of the acid, boils at about 250°. When the acid is warmed with phosphoric chloride, it is converted into phthalic anhydride. It will be seen from the above that the description of this dihydro-acid and its salts given by Graebe and Born (*loc. cit.*) is not quite accurate in some respects.

Dihydrophthalic acid dihydrobromide, $C_8H_{10}Br_2O_4$, is obtained when the dihydro-acid is heated at 100° for 10 hours with an aqueous solution of hydrogen bromide saturated at 0°. It separates from dilute hydrobromic acid in plates melting at 215°, and from water in crystals melting at 200°, which contain 1 mol. H_2O; it is moderately stable towards potassium permanganate, and is converted into hexahydrophthalic acid on reduction with zinc and acetic acid, a fact which proves that the two bromine-atoms are not in the ortho-position to one another.

Dihydrophthalic acid dibromide, $C_8H_8Br_2O_4$, is formed when the

acid is exposed to the vapour of bromine in the dark, and the yellowish product washed with sulphurous acid. It separates from hot dilute alcohol in crystals, melts at 185°, and decomposes on prolonged heating at 100°; it is oxidised by potassium permanganate, but not so quickly as dihydrophthalic acid, into which it is converted on reduction with zinc-dust and acetic acid. The *methyl* salt, prepared by brominating methyl dihydrophthalate, crystallises from methyl alcohol in prisms, and melts at 119°.

All attempts to convert dihydrophthalic acid into isomeric compounds were unsuccessful; it is very stable, and is only slowly acted on by alkalis and acids. It is the only reduction-product of phthalic acid which does not give an anhydride when treated with acetic chloride; it dissolves freely in warm acetic chloride, and on evaporating the solution there remains a colourless, gum-like mass which is completely soluble in sodium carbonate; when heated alone it is converted into phthalic anhydride and benzoic acid, but when warmed with phosphorus oxychloride, it yields an anhydride melting at about 120°, the constitution of which has not yet been determined.

Δ^2 *Tetrahydrophthalic acid* is formed, together with small quantities of the Δ^4 tetrahydro-acid, when phthalic anhydride (5 grams) and crystalline sodium carbonate (10 grams) are dissolved in water (35 c.c.), 3 per cent. sodium amalgam added, and the mixture boiled until the amalgam is completely decomposed; the solution is then slightly acidified with hydrochloric acid, filtered after some time, mixed with excess of dilute sulphuric acid, the precipitated acid separated by filtration, and washed with the least possible quantity of water. The Δ^2 tetrahydro-acid can also be obtained by reducing the dihydro-acid described above in like manner (compare Abstr., 1887, 370), but a larger quantity of the Δ^4 tetrahydro-compound is produced than in the reduction of phthalic acid. The dry, finely-divided crude product is treated with acetic chloride ($3\frac{1}{2}$ parts), the mixture kept for 1—2 days at the ordinary temperature, and the insoluble Δ^4 acid separated by filtration; the solution of the Δ^2 anhydride is evaporated, moisture being excluded, the residue dissolved in ether, and the solution shaken with concentrated potassium carbonate, until it ceases to colour the alkali yellow, in order to free it from traces of the dihydro-acid; the filtered ethereal solution is then evaporated, and the residue recrystallised from water. The Δ^2 acid thus prepared still contains small quantities of a more readily soluble acid, from which it can be separated either by recrystallisation from water, or by fractional precipitation from its alkaline solution, the pure tetrahydro-acid being deposited first in well-defined crystals. It melts at 215° when quickly heated, and is sparingly soluble (1 in 114 at 10°) in water; it combines with bromine (vapour), yielding a saturated *bromide* melting at about 225°. The *methyl* salt is a colourless oil, which forms with bromine a crystalline bromide melting at 73—74°, and also an oily compound.

Δ^2 Tetrahydrophthalic acid is very stable, and is not changed by boiling concentrated alkalis; on oxidation with potassium permanganate in sodium carbonate solution, it seems to yield a more complex acid, which is then decomposed into succinic acid, smaller

quantities of oxalic acid, and an acid which may possibly be glutaric acid. The *anhydride*, prepared as described above, crystallises from ether in prisms, melts at 78—79°, and is reconverted into the acid by hot water. When the acid is heated at its melting point, it is converted into the anhydride, but at the same time the anhydride of the Δ^1 tetrahydro-acid is formed.

Δ^1 *Tetrahydrophthalic acid* is most conveniently obtained by heating the Δ^2 tetrahydro-acid (50 grams), prepared as described above, for about half an hour at 220—230° in a small retort, until water ceases to be eliminated; the brown, crystalline powder is then dissolved in hot water, and the solution evaporated on the water-bath in a tared dish until the weight of the residue is 42 grams. In this way the Δ^1 tetrahydro-acid can be separated from all the other acids, as it alone is converted into its anhydride at 100°. The anhydride is then dissolved in ether, the solution shaken with concentrated potassium carbonate, filtered, and partially evaporated; the crystalline product which is deposited on cooling is extracted with cold light petroleum, the extract evaporated, and the residual anhydride recrystallised from ether. It forms large plates, melts at 74°, and is insoluble in cold, but soluble in hot, water, being thereby converted into the acid; it is readily volatile at 100°, a property which can be made use of to test its purity.

Δ^1 Tetrahydrophthalic acid is very readily soluble in water, from which it separates slowly in large, well-defined, monosymmetric, efflorescent crystals containing 1 mol. H_2O; the damp, crystalline substance melts at a temperature below 100°, being converted into the anhydride, but the dry acid melts at 120°, also with elimination of water. It is identical with the tetrahydrophthalic acid (m. p. 96—100°) obtained by the slow distillation of hydromellitic acid (*Annalen*, **166**, 346); when hydromellitic acid is heated quickly, in small quantities at a time, it gives an oily anhydride, which is probably identical with the anhydride of Δ^3 tetrahydrophthalic acid.

The anhydride of the Δ^1 tetrahydro-acid resembles symmetrical dimethylmaleïc anhydride, not only in appearance, but also in being easily formed from the acid; both anhydrides show, moreover, a great similarity in their behaviour with reagents, and both are volatile at 100°. Concentrated hydrobromic acid at 100° and bromine in the cold have no action on either of the two compounds, although the anhydride of the Δ^1 acid is acted on by bromine at 100°, substitution, and not simple addition, takes place. The acids themselves also show a similar behaviour; pyrocinchonic acid is reduced to dimethylsuccinic acid by sodium amalgam at 100°, Δ^1 tetrahydrophthalic acid being converted into the hexahydro-acid under the same conditions. The methyl salts of both acids combine very readily with bromine. The great resemblance between these two acids and their derivatives, and the great stability of tartrophthalic acid (*Annalen*, **166**, 358), are facts which show that the Δ^1 tetrahydro-acid has doubtless the constitution assigned to it above; this view is confirmed by its behaviour on oxidation. Δ^1 Tetrahydrophthalic acid in sodium carbonate solution is oxidised to adipic acid by 3 per cent. potassium permanganate, but it is much more slowly acted on than any other hydrophthalic or

hydroterephthalic acid, because it does not contain a tertiary hydrogen-atom; it is also less readily oxidised than dimethylmaleïc acid, because an "internal pressure" (compare *Ber.*, **23**, 1281) strengthens the double binding. It undergoes intramolecular change under the influence of potash at a high temperature, being converted into the Δ^2 tetrahydro-acid, but it is not changed when boiled with very concentrated soda, owing to the insolubility of the sodium salt.

Methyl Δ^1 tetrahydrophthalate, prepared by passing hydrogen chloride into a methyl alcoholic solution of the Δ^1 anhydride, is an oil, and combines readily with bromine in ethereal solution, yielding a crystalline substance which consists of two *dibromides*, one of which is readily soluble in cold light petroleum, and crystallises therefrom in plates melting at 83—84°, the other crystallising from a mixture of ether and light petroleum in needles melting at 123—124°. These two compounds are doubtless substitution-products of the maleïnoid and fumaroïd acids; on reduction with zinc-dust and acetic acid, they both yield methyl Δ^1 tetrahydrophthalate. The *dibromide* of the acid cannot be formed directly, but it can be obtained by hydrolysing the dibromide of the methyl salt with hydrobromic acid at 100°; it is a crystalline powder sparingly soluble in water, and on reduction, it is converted into the Δ^1 tetrahydro-acid.

$\Delta^{4\ \mathrm{cistrans}}$ *Tetrahydrophthalic acid* is best prepared by treating the crude product, obtained by the reduction of the dihydro-acid with sodium amalgam, with acetic chloride, as described in the purification of the Δ^2 acid, and after washing the residue with ether, crystallising it from water, in which it is very sparingly soluble. It crystallises in plates, melts at 215—218°, and resembles the fumaroïd hexahydrophthalic acid very closely, from which it can be distinguished by the fact that it decolorises potassium permanganate momentarily; when exposed to the vapour of bromine, it gives a saturated bromide. The *methyl* salt melts at 39—40°, and yields a *dibromide* which crystallises from methyl alcohol in plates melting at 116—117°. The *anhydride* is obtained when the acid is boiled for a long time with acetic chloride; it crystallises from ether in needles and melts at 140°.

The very complete resemblance in physical properties between the Δ^4 tetrahydro-acid and its anhydride with the fumaroïd hexahydro-acid and its anhydride renders it highly probable that both acids contain the group $COOH\cdot\overset{|}{C}H\cdot\overset{|}{C}H\cdot COOH$, from which it follows that the tetrahydro-compound must be either a Δ^3 or a Δ^4 derivative. But since, judging from the behaviour of the analogously constituted Δ^2 tetrahydroterephthalic acid, the Δ^3 tetrahydrophthalic acid should undergo intramolecular change on boiling with soda, the fact that the acid described as Δ^4 tetrahydrophthalic acid is stable under these conditions is evidence that it has the constitution assigned to it.

Δ^3 *Tetrahydrophthalic acid* is deposited in needles when the anhydride of the Δ^4 acid is heated for $2\frac{1}{2}$ hours at 210—220°, the oily product extracted with boiling water, and the solution concentrated by evaporation. It melts at 174°, is readily soluble in water, and is distinguished from all other hydrophthalic acids yet prepared by its

instability towards soda; when boiled therewith for a short time, it is converted into a sparingly soluble, crystalline acid melting at 208°, which consists of a mixture of the Δ^2 and Δ^4 tetrahydro-acids; these two compounds can be separated by treating the finely-divided mixture with acetic chloride. As, further, the Δ^2 acid on heating is partially converted into the Δ^1 anhydride, the double binding can be shifted successively from the Δ^4 to the Δ^3, Δ^2, and Δ^1 position.

The author explains the formation of Δ^3 tetrahydrophthalic acid from the Δ^4 compound by assuming that, on heating the fumaroïd Δ^4 anhydride, it is not only converted into the maleïnoïd modification, but that the double binding shifts from the Δ^4 to the Δ^3 position; arguing from the behaviour of fumaroïd hexahydrophthalic acid, the product should be the maleïnoïd Δ^4 acid, but the fact that it readily undergoes intramolecular change when treated with soda renders it improbable, judging by previous experience, that it is simply the maleïnoïd form of the stable fumaroïd acid, so that it has most probably the constitution assigned to it.

Fumaroïd hexahydrophthalic acid, $C_8H_{12}O_4$, has been previously prepared (*Ber.*, **4**, 276) by reducing the Δ^1 tetrahydro-acid obtained by the distillation of hydropyromellitic acid. It can also be obtained by reducing the dihydrobromide of the dihydro-acid, but it is best prepared by reducing the hydrobromide of crude tetrahydrophthalic acid with sodium amalgam in ice-cold sodium carbonate solution; the product is purified by treating it with a solution of potassium permanganate at the ordinary temperature until the coloration remains permanent for 15 minutes. It crystallises from water in plates very like the crystals of hexahydroterephthalic acid in appearance, and it separates from acetone in long, monosymmetric needles; it is more sparingly soluble in water (1 in 434 at 20°) than any of the other hydrophthalic acids yet prepared. It begins to melt at 215° when quickly heated, and is completely liquefied at 221°. Taking the melting point to be 215°, the following four acids, namely, fumaroïd hexahydro-, Δ^2 and fumaroïd Δ^4 tetrahydro-, and dihydro-phthalic acid have the same melting point. It distils unchanged when quickly heated, but on prolonged heating at a temperature above its melting point, water is eliminated, and it is partially converted into the anhydride of the maleïnoïd acid; its solution in hot sodium carbonate gradually decolorises potassium permanganate, but no action takes place in the cold. The calcium salt is characterised by being very sparingly soluble. The *methyl* salt, $C_8H_{10}O_4Me_2$, melts at 33°, and is moderately easily soluble in light petroleum. The *anhydride*, $C_8H_{10}O_3$, prepared by warming the acid with acetic chloride, crystallises from ether in long needles and melts at 140°. When the acid is warmed with bromine (2 mols.) and phosphoric chloride for six hours, it is converted into a syrup which, on reduction with zinc-dust and acetic acid, yields a sparingly soluble acid resembling the Δ^2 tetrahydro-acid, and some readily soluble products, but the Δ^1 tetrahydro-acid is not obtained. The anhydride shows a like behaviour.

Maleïnoïd hexahydrophthalic acid is obtained when the anhydride of the fumaroïd acid is heated for seven to eight hours at 210—220°, the product dissolved in water, the solution evaporated to dryness,

and the residual acid treated with potassium permanganate in alkaline solution until a permanent coloration is produced. It crystallises from water, in which it is more readily soluble than the isomeride, in four-sided prisms, sinters together at about 182°, and melts at 192°. It behaves like the fumaroïd acid with potassium permanganate, and when heated with concentrated hydrochloric acid at 180°, it is reconverted into the fumaroïd modification. The barium salt and the zinc salt are more sparingly soluble in hot than in cold water. The *anhydride* is formed when the acid is heated to its melting point; it boils at 145° (18 mm.) and melts at 32°.

When Δ^1 tetrahydrophthalic acid is reduced with sodium amalgam, a mixture (m. p. 183°) of the two hexahydro-acids is obtained, but the two compounds cannot easily be separated by recrystallisation from water. This fact explains why the hexahydro-acid obtained by the reduction of the Δ^1 tetrahydro-acid with sodium amalgam is quite different in appearance from that obtained by reducing the same compound with hydriodic acid (compare *Annalen*, **166**, 350).

F. S. K.

The Constitution of Benzene. By A. Claus (*J. pr. Chem.* [2], **42**, 260—267).—A reply to Baeyer's last publication on the same subject (preceding abstract), and chiefly of a personal nature.

H. G. C.

Symmetrical Alkylisophthalic Acids. By O. Doebner (*Ber.*, **23**, 2377—2381).—The formation of uvitic acid from pyruvic acid is due to the decomposition of part of the pyruvic acid into acetaldehyde and carbonic anhydride, and to the subsequent condensation of the aldehyde with the remaining acid. If some other aldehyde is employed, corresponding homologues of uvitic acid are obtained; the reaction probably takes place in two stages:—$3COMe{\cdot}COOH$ + $R{\cdot}CHO = RC{<}^{CH{:}C(COOH)}_{CH{\cdot}C(COOH)}{>}C{\cdot}CO{\cdot}COOH + 3H_2O + H_2$; by the action of barium hydroxide on this hypothetical intermediate product, oxalic acid is eliminated, and the symmetrical acid

$$C_6H_3R{\cdot}(COOH)_2$$

is produced.

Ethylisophthalic acid, $C_6H_3Et(COOH)_2$, is prepared by boiling crystallised barium hydroxide (120 grams) with pyruvic acid (50 grams) and propaldehyde (16 grams) for eight hours in a reflux apparatus; the product is filtered whilst hot, and the residue boiled out several times with water; the combined filtrates are then evaporated, and excess of hydrochloric acid added; the precipitate, when treated with hot water and crystallised from dilute alcohol, forms colourless plates which melt at 263—264°, and at higher temperatures sublime with partial decomposition. It is readily soluble in alcohol, ether, benzene, and glacial acetic acid, but very sparingly in water, and is insoluble in light petroleum. The salts of the *alkali metals* and the *calcium*, *barium*, and *magnesium salts* readily dissolve in water; the *lead*, *copper*, and *silver salts* are less soluble. The calcium salt yields ethylbenzene on heating.

Isopropylisophthalic acid, $C_6H_3Pr^{\beta}(COOH)_2$, is formed from iso-

butaldehyde and pyruvic acid in a manner similar to the ethyl-derivative, which it closely resembles; it crystallises from dilute alcohol or acetic acid in colourless plates melting at 275—276°.

Isobutylisophthalic acid, $C_4H_9{\cdot}C_6H_3(COOH)_2$, is obtained from isovaleraldehyde; it crystallises in colourless, lustrous plates which melt at 260°.

Phenylisophthalic acid, $C_6H_3Ph(COOH)_2$, is prepared from benzaldehyde and pyruvic acid; it is more sparingly soluble than the preceding compound, but may be crystallised from glacial acetic acid; it melts above 310°. The *barium salt* dissolves very sparingly in hot water. Diphenyl is obtained on heating the calcium salt. The constitution of the above compounds is proved by the fact that isobutylisophthalic acid yields trimesic acid on oxidation. J. B. T.

Derivatives of Phenyl Salicylate (Salol). By W. KNEBEL (*J. pr. Chem.* [2], **42**, 158).—*Phenyl nitrosalicylate*,

$$NO_2{\cdot}C_6H_3(OH){\cdot}COOPh,$$

is obtained when nitric acid is dropped into a warm solution of phenyl salicylate in glacial acetic acid; it forms lustrous needles melting at 150°, sparingly soluble in alcohol, more freely in glacial acetic acid. On hydrolysis, it yields metanitrosalicylic acid (m. p. 222°) and phenol; when heated with strong ammonia, it yields nitrosalicylamide.

Phenyl dinitrosalicylate is obtained by heating the glacial acetic acid solution of phenyl salicylate with nitric acid (sp. gr. 1·52) for some time on the water-bath; it crystallises in needles which melt at 183° and are soluble in glacial acetic acid.

Phenyl trinitrosalicylate, obtained when phenyl salicylate is added to nitric acid of sp. gr. 1·52, crystallises in silvery scales melting at 100° and easily soluble in alcohol. A. G. B.

Derivatives of Paratolylglycin. By C. A. BISCHOFF and A. HAUSDÖRFER (*Ber.*, **23**, 1997—2002).—Paratolylglycin,

$$C_6H_4Me{\cdot}NH{\cdot}CH_2{\cdot}COOH,$$

is readily obtained in quantity by heating chloracetic acid and paratoluidine with sodium acetate, and recrystallising the product from hot water. In an attempt to convert it into paraditolyl-$\alpha\gamma$-diketopiperazine, it was heated first at 110—120° and subsequently at 200°, the product washed with ether, recrystallised from alcohol, and boiled with ammonia to remove any unaltered glycin. The product was, however, found to be *paratolylglycinimide*, $NH(CO{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4Me)_2$, melting at 208—210°. It is probable that the anhydride is first formed, and that this is converted by ammonia into the imide. The latter is very stable, not being decomposed by boiling acids and alkalis. If, however, paratolylglycin is heated at 230—250° instead of the lower temperature mentioned above, it is converted into *paraditolyl-$\alpha\gamma$-diketopiperazine*, which, after recrystallisation from acetic acid, melts at 254°. By the action of acetic anhydride, paratolylglycin yields a compound melting at 219—222°, the composition of which has not yet been determined.

Paratolylphenyl-αγ-diketopiperazine, $C_6H_4Me{\cdot}N{<}{}^{CH_2{\cdot}CO}_{CO{\cdot}CH_2}{>}NPh$, is obtained by heating bromacetylphenylglycin with paratoluidine and sodium acetate. It forms colourless needles melting at 220—221°, and insoluble in alkalis. An attempt was made to obtain an isomeric piperazine by the action of aniline on chloracetoparatoluidide, but the compound formed was fonnd to be *chloroacetotoluidide*, $C_6H_4Me{\cdot}NH{\cdot}CO{\cdot}CH_2Cl$, which, on treatment with aniline and sodium acetate, yields *phenylglycinparatoluidide*,

$$C_6H_4Me{\cdot}NH{\cdot}COCH_2{\cdot}NHPh,$$

melting at 165°.

By the action of paratoluidine, chloracetic acid, and sodium acetate, *paratolylimidodiacetic acid*, $C_6H_4Me{\cdot}N(CH_2{\cdot}COOH)_2$, is formed, but decomposes so readily that it could not be obtained pure. On treatment with toluidine, it yields the *monotoluidide* melting at 222°, and a substance which is probably the impure *ditoluidide*. The first compound may also be obtained from paratolylglycintoluidide and chloracetic acid. H. G. C.

Derivatives of Orthotolylglycin. By C. A. Bischoff and A. Hausdörfer (*Ber.*, **23**, 1991—1996).—Orthotolylglycin is converted by the method previously given (Abstr., 1889, 1011) into *orthoditolyl-αγ-diketopiperazine*, $C_6H_4Me{\cdot}N{<}{}^{CH_2{\cdot}CO}_{CO{\cdot}CH_2}{>}N{\cdot}C_6H_4Me$, the yield obtained being 63·6 per cent. Abenius and Widman were unable to obtain any piperazine in this manner. By the action of the gases evolved from arsenious oxide and nitric acid on this compound dissolved in cooled sulphuric acid, a substance is obtained, mixed with other bye-products, which does not give Liebermann's reaction, and appears to have the constitution $NO_2{\cdot}C_6H_3Me{\cdot}N{<}{}^{CH_2{\cdot}CO}_{CO{\cdot}CH_2}{>}N{\cdot}C_6H_3Me{\cdot}NO_2$. It is purified by extraction with boiling chloroform and recrystallisation from acetic acid, and melts at 253—254°. If the sulphuric acid is not cooled, two other compounds are formed, neither of which gives Liebermann's reaction; they have the formulæ $C_{18}H_{16}N_5O_8$ and $C_{18}H_{16}N_5O_6$, and melt at 262—265° and over 300° respectively.

Orthotolylimidodiacetic acid, $C_6H_4Me{\cdot}N(CH_2{\cdot}COOH)_2$, is prepared by boiling tolylglycin (1 mol.) with chloracetic acid (1 mol.), sodium carbonate ($1\frac{1}{2}$ mols.), and a little water in a reflux apparatus. It separates from a mixture of alcohol and light petroleum in lustrous, white crystals, which melt at 158—162° with decomposition, and are insoluble in water, dilute hydrochloric acid, alkalis, and light petroleum, sparingly soluble in ether, more readily in alcohol and chloroform. On treatment with toluidine, it yields the *mono-* and *di-toluidide*, the first of which forms crystals melting at 146—148°, whilst the second melts at 149—150°. The monotoluidide, unlike the corresponding compound in the phenyl-group, does not yield a piperazine on boiling with acetic anhydride, but is converted into *diorthotolylcarbamide*, $CO(NH{\cdot}C_7H_7)_2$.

Phenylorthotolyl-αγ-diketopiperazine, $PhN<\genfrac{}{}{0pt}{}{CH_2\cdot CO}{CO\cdot CH_2}>N\cdot C_6H_4Me$, was obtained by Abenius by the action of aniline on chloracetylorthotolylglycin. It may also be obtained by heating orthotoluidine with chloracetylphenylglycin and sodium acetate. H. G. C.

Compounds of Glycuronic Acid. By E. Külz (*Zeit. Biol.*, **27**, 247—258).—*Phenylglycuronic acid*, $C_6H_{11}PhO_7$, was prepared in the following way:—Animals were dosed with phenol, and the urine, which was of a dark tint, collected and evaporated on the water-bath to a thin syrup. A mixture of 1 litre of ether, 500 c.c. of 90 per cent. alcohol, 30 c.c. of sulphuric acid (concentrated sulphuric acid and water in equal parts) was repeatedly shaken with this until no more lævorotatory substance passed into solution. The ether and alcohol were distilled off from the extract, the residue carefully neutralised with barium hydroxide, the barium sulphate filtered off, and the filtrate precipitated first with lead acetate and then with basic acetate; the precipitate produced by the latter was well washed, suspended in water, and decomposed with hydrogen sulphide, the lead sulphide filtered off, and the excess of gas driven off from the filtrate by gentle heat. On evaporation of this solution to a thin syrup, it deposited crystals of phenylglycuronic acid, which were dissolved in warm water, the solution decolorised by animal charcoal, and the crystals once more obtained on evaporation were purified by repeated recrystallisation. The crystals were long needles, resembling asbestos, burnt without residue, sublimed slowly below 100°, were charred at 100°, and melted approximately at 148°. Their solution was lævorotatory and reduced Fehling's solution. Their barium salt could not be prepared in a crystalline form, but the potassium and sodium salts crystallised from an aqueous solution. A 3 per cent. aqueous solution of the acid was distilled with sulphuric acid for three hours; it became yellow; the distillate contained phenol; the residue still reduced Fehling's solution powerfully, and was dextrorotatory; barium glycuronate was prepared from it by the method of Schmiedeberg and Meyer (*Zeit. physiol. Chem.*, **3**, 442).

The preparation of the following compounds of glycuronic acid was, *mutatis mutandis*, the same as that just described.

Quinolglycuronic acid is lævorotatory, and non-crystalline. Its barium, potassium, and sodium salts are also non-crystalline. On distillation with sulphuric acid, quinol was found in the distillate, and glycuronic acid in the residue.

Resorcinolglycuronic acid is lævorotatory, crystalline, and reduces Fehling's solution; its barium salt was also obtained in a crystalline form. On distillation with sulphuric acid, benzoic acid was found in the distillate, glycuronic acid in the residue.

Thymolglycuronic acid is lævorotatory, crystalline, and non-reducing. Its barium salt was crystallised. On distillation with sulphuric acid, very small quantities of thymol were obtained in the distillate. Thymol appears to be to a great extent decomposed by sulphuric acid, yielding an oil which smells like thymol. Glycuronic acid, as in the previous cases, was found in the residue.

Turpentineglycuronic acid has been noted in the urine of patients by previous observers. It is amorphous, lævorotatory, soluble in water and in alcohol, soluble with difficulty in ether. The barium, potassium, sodium, and silver salts are amorphous. The acid only reduces Fehling's solution after prolonged boiling. On distillation with sulphuric acid, the residue contained glycuronic acid, and the distillate, oil of turpentine. W. D. H.

So-called Anilinetrisulphonic Acid. By C. L. JACKSON and G. T. HARTSHORN (*Ber.*, **23**, 2143).—The acid previously described as anilinetrisulphonic acid (Abstr., 1888, 1093) has now been found to be anilinesulphonic acid (sulphanilic acid). F. S. K.

Nitrocymenesulphonic Acids. By G. ERRERA (*Gazzetta*, **19**, 533—545).—*Nitro-α-cymenesulphonic acid*, $HSO_3 \cdot C_6H_2MePr \cdot NO_2$ [2 : 1 : 4 : 6]. Cymene from camphor (100 grams) is dissolved in concentrated sulphuric acid (3 vols.); on cooling, the solution separates into two layers, the lower of which is rejected; a solution of nitric acid (58 grams, sp. gr. = 1·51) in an equal volume of concentrated sulphuric acid is gradually mixed with the residue, the mass being meanwhile kept cold; it is then heated, diluted, neutralised with barium carbonate, and concentrated. Nodules of barium nitro-α-cymenesulphonate are deposited, and when recrystallised form nodules consisting of yellow or reddish needles, or thin plates containing 1 mol. H_2O, and only slightly soluble in cold water. The mother liquor eventually settles into a viscid mass. The *magnesium salt* forms white, crystalline nodules containing 5 mols. H_2O; the solutions of both barium and magnesium salts are coloured red by the light.

The acid is prepared from the barium salt; it is a heavy, brown liquid which sets into a crystalline mass when kept for some time over sulphuric acid in a vacuum, but deliquesces on exposure to the air. Both the acid and its salts deflagrate when heated to 200°, leaving a mass of spongy carbon; this occurs even in presence of water.

Nitro-α-cymenesulphonamide, $SO_2NH_2 \cdot C_6H_2MePr \cdot NO_2$ [2 : 1 : 4 : 6]. —The barium salt of the preceding acid is dehydrated at 170°, heated with phosphoric chloride, and the viscid product thrown into water; the chloride of the acid radicle separates in the form of a heavy, oily liquid which combines energetically at the ordinary temperature with a saturated solution of ammonia; on cooling and recrystallising the product from dilute alcohol, the amide is obtained in micaceous scales melting at 138—139°, and readily soluble in alcohol and in hot water.

Amido-α-cymenesulphonic acid, $HSO_3 \cdot C_6H_2MePr \cdot NH_2 + H_2O$ [2 : 1 : 4 : 6], is prepared by reducing nitro-α-cymenesulphonic acid with ammonium sulphide. It crystallises from boiling water in hard, brittle, brilliant, pale-yellow prisms containing 1 mol. H_2O; when its solution is rapidly cooled, it forms tables or a white powder. When heated on platinum-foil, it chars and decomposes without melting.

The salts which this acid forms with the alkalis and alkaline earths are all extremely soluble in water.

Chloro-α-cymenesulphonic acid, $HSO_3 \cdot C_6H_2MePrCl$ [2 : 1 : 4 : 6], is prepared by a modification of Sandmeyer's reaction; the powdered amido-acid is suspended in a boiling solution of cuprous chloride in hydrochloric acid, and a current of nitrous acid passed in until solution is complete. The *barium salt* forms very thin, colourless plates containing 3 mols. H_2O. *Bromo-α-cymenesulphonic acid* is obtained like the chlorinated derivative. The *barium salt* contains only 1 mol. H_2O. On heating chlorocymenesulphonic acid at 180° with fuming hydrochloric acid, and distilling the product in a current of steam, the distillate contains drops of a chlorocymene, which, on oxidation with nitric acid (sp. gr. = 1·29), yields needles of metachloroparatolnic acid, $C_6H_3MeCl \cdot COOH$ [1 : 6 : 4], melting at 196—197°. The chlorocymene must, therefore, have the constitution [Me : Pr : Cl = 1 : 4 : 6] (Abstr., 1887, 37; 1889, 495); this, in conjunction with the circumstance that in Sandmeyer's reaction, chlorine takes the position of the amidogen, and that α-cymenesulphonic acid forms the starting point of the above compounds, establishes the constitutions ascribed to them. Amidocymenesulphonic acid is thus isomeric with Widman's cymidinesulphonic acid, $HSO_3 \cdot C_6H_2MePr \cdot NH_2$ [2 : 1 : 4 : 5] (Abstr., 1886, 470), from which it differs in only slowly giving up its water of crystallisation even at 120—130°, whilst the latter becomes anhydrous at 110—115°; barium cymidinesulphonate, moreover, crystallises with $2\frac{1}{2}$ mols. H_2O.

It was mentioned before that the mother liquor from the barium nitro-α-cymenesulphonate congeals to a viscid mass; this mass contains barium salts too impure to crystallise. By treatment with magnesium sulphate, yellow prisms of a *magnesium* salt,

$$[C_6H_2MePr(NO_2) \cdot SO_3]_2Mg + 6H_2O,$$

were isolated. From this a *barium* salt containing 5 mols. H_2O, and crystallising in yellow plates, was prepared. These substances are salts of an isomeric nitrocymenesulphonic acid which is now under investigation. S. B. A. A.

Formation of Acid Chlorides by the Action of Sulphonic Monochloride. By G. CARRARA (*Gazzetta*, 19, 499—504).—In view of the discordant observations of this reaction by Knapp (*Zeit. für Chem.*, 1869, 41), Armstrong (this Journal, 1871, 173), Beckurts and Otto (Abstr., 1879, 229), Spica (Abstr., 1881, 602), Paternò and Canzoneri (Abstr., 1881, 593), and by the author, the action of sulphonic monochloride on chlorocymene was investigated. Amounts corresponding respectively with 1 and 2 mols. of the former to 1 mol. of the latter were maintained at 98—100° until the evolution of hydrogen chloride had almost ceased, the product treated with excess of hot water, washed, and dried at 100°. In both experiments, the product consists of chlorocymenesulphonic chloride, $C_{10}H_{12}Cl \cdot SO_2Cl$, but the yield from the double proportion of sulphonic chloride is more than five times as great as that from the single quantity. This difference is attributed to a secondary action of sulphonic chloride on the chlorocymene-

sulphonic acid first formed. To confirm this view, the acid was directly treated with sulphonic chloride, and a yield of 56 per cent. of the acid chloride obtained. The equation $C_{10}H_{12}Cl{\cdot}SO_2{\cdot}OH + SO_2Cl{\cdot}OH = C_{10}H_{12}Cl,SO_2Cl + H_2SO_4$ therefore affords a more probable representation of the formation of the acid chlorides than that given by Beckurts and Otto (*loc. cit.*). The author confirms Paternò and Canzoneri's observation that bromocymenesulphonic chloride is not affected by the action of water, but is converted into the sulphonic acid by boiling with alcohol. It is found, however, that if the solutions of acid chloride and alcohol are only heated together for $1\frac{1}{2}$ hours, and allowed to evaporate spontaneously, a deposit of white, pointed, prismatic crystals of an *ethyl salt*, $C_{10}H_{12}Cl,SO_3Et$, forms after a few days. The crystals melt at 42—43°, and, unlike the sulphonic acid, only dissolve very partially in water after prolonged boiling, a portion passing over with the steam; they dissolve in ether and benzene, and volatilise with decomposition at about 110—120°. The presence of this intermediate compound explains the conversion of the acid chloride into the sulphonic acid, which, probably, takes place in two stages as follows:—

$$(1.)\ C_{10}H_{12}Cl{\cdot}SO_2Cl + EtOH = C_{10}H_{12}Cl{\cdot}SO_3Et + HCl$$
$$(2.)\ C_{10}H_{12}Cl{\cdot}SO_3Et + H_2O = C_{10}H_{12}Cl{\cdot}SO_3H + EtOH.$$

S. B. A. A.

Dibenzamide. By F. KRAFFT (*Ber.*, **23**, 2389—2393).—Dibenzamide is prepared by treating benzoic chloride (16 grams) with benzonitrile (30 grams) and aluminium chloride (16 grams) for some time at 100°; the solid product is treated first with water, then with dilute alcohol, and finally with dilute sodium hydroxide solution; the insoluble residue consists of kyaphenine. On adding excess of hydrochloric acid to the alkaline filtrate, a precipitate is formed, which is purified by dissolving in warm alcohol and adding water; the yield is fairly large. Dibenzamide crystallises in lustrous needles melting at 147—148°; on distillation, even under reduced pressure, it decomposes into benzonitrile and benzoic acid.

Benzoic acid and benzamide are produced by boiling dibenzamide for a day with a large excess of water. Dilute acids act in the same way, only more rapidly. Dibenzamide readily dissolves in cold dilute sodium hydroxide solution, and is precipitated unchanged by the immediate addition of hydrochloric acid; but if the alkaline solution is allowed to remain for some time, benzamide and sodium benzoate are formed (compare Bath and Senhofer, Abstr., 1876, 417).

Sodium dibenzamide may be prepared by digesting dibenzamide with sodium wire in anhydrous ether for 1—2 days. *Silver dibenzamide*, $NAgBz_2$, is obtained as a flocculent, crystalline precipitate on adding a cold, aqueous solution of silver nitrate to an ammoniacal solution of dibenzamide in alcohol. Ethyl benzoate and benzamide are formed on boiling dibenzamide with alcohol for some time.

J. B. T.

Benzenesulphoneorthamidobenzamide and its Anhydride. By E. FRANKE (*J. pr. Chem.* [2], **42**, 271—272).—Benzenesulphone-

orthamidobenzamide is readily obtained by the action of benzenesulphonic chloride on orthamidobenzamide, and crystallises from benzene or hot water in white needles melting at 166°. On warming with concentrated hydrochloric acid, it yields a *hydrochloride*, $C_{13}H_{12}N_2SO_3,HCl$, crystallising in white needles. The free base readily passes into the anhydride, which crystallises from alcohol in white needles melting at 145—146°, and scarcely soluble in hot water. It also forms salts in which one atom of hydrogen is displaced by metal, and, on warming with potash and methyl iodide in alcoholic solution, yields the compound $C_{13}H_9MeN_2SO_2$, crystallising in needles which melt at 116°. H. G. C.

Diphenylacetylenediureïne and some of its Derivatives. By A. ANGELI (*Gazzetta*, **19**, 563—568).—Schiff (Abstr., 1877, 885) and Franchimont and Klobbie (Abstr., 1889, 125) have examined the action of urea and ureïdes on the diketones and dialdehydes of the fatty acids; the author has now extended those experiments to some members of the aromatic group.

Diphenylacetylenediureïne, $C_{15}H_{11}O_2N_4$, is prepared by heating a mixture of benzile with 3 times its weight of carbamide at 220° for about 15 minutes. The portion of the product insoluble in hot alcohol is crystallised from glacial acetic acid. It forms a white, silky powder which does not melt at 310°. When heated on platinum foil, it gives off white fumes and melts to a dark mass. It is insoluble in water and in benzene, but readily soluble in boiling glacial acetic acid, and slightly in hot alcohol. It dissolves in concentrated sulphuric acid, and is reprecipitated unchanged on dilution. It yields no salts, and is insoluble in alkaline liquids; with ammoniacal silver nitrate, a black precipitate is obtained consisting chiefly of reduced silver. It is formed by the condensation of 2 mols. of carbamide with 1 of benzile, and, probably, has the constitution $CO<\begin{matrix}NH\cdot PhC\cdot NH\\ | \\ NH\cdot PhC\cdot NH\end{matrix}>CO$. It only forms one *acetyl-derivative*, $C_{16}H_{12}N_4O_2Ac_2$, which crystallises in spherical tufts of pale-violet needles, melting with decomposition at 266°; it is insoluble in water, and only slightly soluble in alcohol. The solutions in ethyl acetate and in acetic acid are colourless by transmitted light, but exhibit a very marked violet fluorescence; the hot alcoholic solution is decomposed by potash, with separation of the original diureïne.

When the diureïne is heated with sodium acetate and acetic anhydride for eight hours at 240°, a substance is formed having the composition $C_{15}H_{12}N_2O$. The solutions of this compound in acetic acid and in ethyl acetate likewise exhibit a violet fluorescence. It is insoluble in water and in benzene. It is probably a product of decomposition of the acetyl-derivative, and is either identical or polymeric with the compound $CO<\begin{matrix}NH\cdot CPh\\ \| \\ NH\cdot CPh\end{matrix}$. The diacetyl-derivative seems to have the constitution $CO<\begin{matrix}NH\cdot CPh\cdot NAc\\ | \\ NH\cdot CPh\cdot NAc\end{matrix}>CO$.

S. B. A. A.

Note.—The term "ureïne" is used by Franchimont and Klobbie to denote that class of ureïdes in which each NH-group is attached to a hydrocarbon residue and neither lies between two CO-groups; such ureïdes yield dinitro-derivatives (Abstr., 1889, 125).

Monophenylthiocarbamide and Imidothiocarbamates. By A. BERTRAM (*Inaugural Dissertation, Chem. Centr.*, 1890, i, 939—941). —*Methyl imidophenylthiocarbamate*, NHPh·C(NH)·SMe, melting at 71°, is prepared by the action of methyl iodide on monophenylthiocarbamide, as hydriodide, from which the free base is obtained by the action of sodium carbonate and extraction with ether; the hydroiodide melts at 147°. It forms two sulphates, $2C_8H_{10}N_2S,H_2SO_4$ and $C_8H_{10}N_2S,H_2SO_4$, both melting at 171°; the nitrate melts at 113°; the acetate at 115°; the picrate at 175°; the platinochloride at 184°. For the determination of the constitution of the base the following reactions were made. By means of dry distillation, it was decomposed into aniline, methyl mercaptan, and an unknown compound. Heated with carbon bisulphide at 140—150°, aniline, hydrogen thiocyanate, and phenylthiocarbimide were obtained. When heated with dilute sulphuric acid at 160°, the base yields *methyl phenylthiocarbamate*, NHPh·CO·SMe, melting at 84—85°, from which the constitution of the base is proved. With methyl iodide, the base forms an additive compound melting at 184° which, with sodium carbonate, yields a new base, *methyl imidomethylphenylthiocarbamate*, NPhMe·C(NH)·SMe. If this base is heated with dilute sulphuric acid at 160°, *methyl methylphenylthiocarbamate*, NPhMe·CO·SMe, is formed melting at 54°, which proves the constitution of the new imido-base. This base is an oil, and the picrate melts at 139°. With carbon bisulphide, it forms hydrogen thiocyanate, methyl mercaptan, phenylthiocarbimide and another substance melting at 84°. Methyl iodide reacts with methyl imidomethylphenylthiocarbamate with formation of an additive compound, the hydriodide of *methyl methylimidomethylphenylthiocarbamate*, from which the free base, NPhMe·C(NMe)·SMe, is obtained by the action of sodium carbonate. This base is an oil, the hydriodide of which melts at 184°, the picrate at 126°, and the platinochloride at 174°. Heated with carbon bisulphide at 160°, the base yields phenylthiocarbimide, and *methyl methylphenyldithiocarbamate*, NPhMe·CS·SMe, melting at 88°. With sulphuric acid, methyl methylphenylthiocarbamate is again obtained.

Methyl-symmetrical-diphenylthiocarbamide and methyl iodide combine with formation of the hydriodide of *methyl phenylimidomethylphenylthiocarbamate*, from which the free base may be obtained. With carbon bisulphide, it forms methyl methylphenyldithiocarbamate.

Ethyl iodide unites with monophenylthiocarbamide yielding the compounds corresponding with those which it forms with methyl iodide; *ethyl imidophenylthiocarbamate*, NHPh·C(NH)·SEt, is an oil; the hydriodide melts at 103°, and the picrate at 196°. Ethyl iodide combines with it, forming *ethyl imidoethylphenylthiocarbamate*, NPhEt·C(NH)·SEt; the picrate melts at 170°. If this is heated with ethyl iodide, it forms *ethyl ethylimidoethylphenylthiocarbamate*,

NPhEt·C(NEt)·SEt, an oil which boils at 273° with slight decomposition; the picrate melts at 96°, the platinochloride at 135°.

Ethylene bromide reacts with monophenylthiocarbamide with formation of the compound $C_{16}H_{18}N_4S$, which is probably ethylene imidophenylthiocarbamate. The hydrobromide melts at 214°, the free base at 139°, the hydrochloride at 218°, the platinochloride at 150°, and the picrate at 196°. If the base is heated above 139°, ethylene mercaptan separates, from which it appears that the base is an imidocarbamate. If heated with carbon bisulphide, hydrogen thiocyanate, ethyl mercaptan, aniline, and an unrecognisable compound are produced.

The halogens decompose the above compounds, oxidising the thioalcohol group to the sulphonic-acid group, and convert the remainder into a dihalogen- and then into a trihalogen-carbamide, the latter yielding α-trihalogen aniline. Methyl imidophenylthiocarbamate is converted by bromine into methylsulphonic acid, tribromaniline, tribromophenylcarbamide, and dibromophenylcarbamide.

J. W. L.

Preparation of Aromatic Sulphides and of Thioxanthone. By J. H. Ziegler (*Ber.*, **23**, 2469—2472).—By the action of diazo-compounds on sodium phenyl mercaptan, corresponding sulphides are obtained. The reaction is best carried out at a temperature of 60—70°, in order to avoid the formation of explosive diazo-derivatives. The phenyl sulphides from diazo-ortho- and para-toluene, and diazo-2-naphthalene, are viscid liquids boiling at 290—310°. *Phenyl-1-naphthyl sulphide* crystallises in plates melting at 49°. *Para-acetamidodiphenyl sulphide*, from paradiazoacetanilide, is deposited from water in white crystals melting at 144°. The free *base* is obtained by hydrolysis; it crystallises from alcohol in brownish needles melting at 97°. *Diphenylsulphideorthocarboxylic acid* is prepared by the action of alkalis on the product obtained from sodium phenyl mercaptan and diazobenzoic acid; it is deposited from benzene in white plates, which melt at 165·5°. On treatment with concentrated sulphuric acid, the compound dissolves with a very characteristic light-green fluorescence, and, on pouring into cold water, *thioxanthone* is precipitated; it is best purified by sublimation. It crystallises in almost colourless needles melting at 207°, and boiling at 371—373° under a pressure of 715 mm. It is readily soluble in benzene, glacial acetic acid, and carbon bisulphide, and is not acted on by hydroxylamine or phenylhydrazine.

J. B. T.

Methyl-derivatives of Indole. By C. Zatti and A. Ferratini (*Ber.*, **23**, 2302—2307).—When indole or α-methylindole is heated with methyl iodide, the hydriodide of trimethyldihydroquinoline is formed, and not of dimethyldihydroquinoline as Fischer and Steche thought (Abstr., 1888, 298). When the base derived from this is heated with methyl iodide, the same trimethyldihydroquinoline hydriodide, $C_{12}H_{15}N,HI$, melting at 253°, is again obtained. At the same time, however, a more soluble salt, of the composition $C_{14}H_{19}N,HI$, is also formed, the reaction taking place according to the equation $2C_{12}H_{15}N + 2MeI = C_{12}H_{13}Me_2N,HI + C_{12}H_{15}N,HI$. Tri-

methyldihydroquinoline is heated for three hours at 100° in a sealed tube, with excess of methyl iodide; the contents of the tube, after evaporation of the methyl iodide, are washed with ether and separated by fractional crystallisation from alcohol into trimethyldihydroquinoline hydriodide and the penta-methyl compound, which is perhaps the methiodide compound of tetramethyldihydroquinoline. This is a pale-red, crystalline powder melting at 169°, dissolving easily in water and alcohol, but not in ether and ethyl acetate. Potash liberates the base, which is a colourless oil soluble in ether, and turning red in the air. It dissolves easily in dilute acids, and is precipitated from a strong hydrochloric acid solution by ferric chloride. The platinochloride forms pale-yellow needles.

The trimethyldihydroquinoline has the constitution $C_9H_6Me_3N$ [$Me_3 = 1' : 3' : 4'$, $\Delta = 3' : 4'$]; that of the pentamethyl-derivative is not yet determined. C. F. B.

Nitrosoindole. By C. Zatti and A. Ferratini (*Ber.*, **23**, 2299—2302).—To a cooled solution of indole (3 grams) in 90 per cent. acetic acid (100 grams), a concentrated solution of sodium nitrite (2 grams) is added, and the liquid poured into ice and water. The red precipitate is dried over sulphuric acid and treated with ethyl acetate; part dissolves, and part does not. The insoluble portion is dissolved in acetone, decolorised with animal charcoal, and precipitated with light petroleum. By this means brilliant, small, yellow crystals (1·3 gram) melting with decomposition at 171—172° are obtained. These are insoluble in water, ether, light petroleum, and benzene, but easily soluble in warm acetone. In acids they dissolve with partial decomposition, and give reddish solutions, which deposit reddish precipitates when diluted with water. With strong potash, they give a red solution, which deposits a red precipitate when acidified. They show all the nitroso-reactions, explode gently when ignited, yield Liebermann's colouring matters with phenol and sulphuric acid, and again form indole when reduced. All the reactions agree with the formula $CH{<}{\scriptstyle CH- \atop \scriptstyle C_6H_4}{>}N{\cdot}NO$ for true nitrosoindole, but the high melting point leads one to suspect that it is a polymeride.

That part of the original precipitate which dissolves in ethyl acetate is identical with Nencki's nitroso-product, obtained by treating a saturated aqueous solution of indole with fuming nitric acid. It appears, however, not to be a true nitrosamine. C. F. B.

Synthesis of β-Indolecarboxylic Acid. By C. Zatti and A. Ferratini (*Ber.*, **23**, 2296—2298).—To prepare this acid, indole (5 grams) is heated for three to four hours at 230—250°, and finally to 300° with sodium (1 gram) in a small retort through which a current of carbonic anhydride is passed. Alcohol is then added to remove the excess of sodium, the excess of alcohol evaporated, and the residue distilled with steam, so as to drive over the unaltered indole; the sodium salt of β-indolecarboxylic acid remains in the solution. The acid is precipitated on acidifying the liquid, dissolved in sodium carbonate, again liberated, and then purified by dissolving it in ethyl

acetate and precipitating it with light petroleum. Its properties agree with those formerly described, except that when pure it melts at 218°, and not at 214°. A very small quantity of the α-acid is also formed in this reaction.

β-Indolecarboxylic acid, unlike the α-acid, yields no imine-anhydride when heated with acetic anhydride, but forms a mixed anhydride of β-indolecarboxylic and acetic acids, $C_8H_6N{\cdot}CO{\cdot}O{\cdot}COMe$. It will be remembered that an analogy to this exists among the pyrroline-derivatives; the α-carboxylic acids of this series yield imine-anhydrides, whilst the β-acids do not. C. F. B.

Constitution of Apiole and its Derivatives. By G. CIAMICIAN and P. SILBER (*Ber.*, 23, 2283—2295).—*Apionileglyoxylic* (*Apioneketonic*) *acid*, $COOH{\cdot}CO{\cdot}C_6H(OMe)_2{<}^{O}_{O}{>}CH_2$, is formed, together with apiolic acid, when isoapiole is oxidised with alkaline permanganate, and is obtained on acidifying the solution, filtering it from precipitated apiolic acid, and extracting the filtrate with ether. It is soluble in water, ether, acetic acid, and boiling benzene, and crystallises from water in long, yellowish needles, which have no definite melting point, but decompose between 160° and 172°. It combines with phenylhydrazine hydrochloride, and its silver salt forms a white, crystalline precipitate.

When isoapiole is dissolved in alcohol and reduced with sodium, a *dihydroapiole*, $C_{12}H_{16}O_4$, is formed, and is precipitated when the solution is diluted with water. It melts at 35°, and boils at 292°, dissolves in ether, benzene, light petroleum and alcohol, and with strong sulphuric acid gives first a yellow and then a red solution. In addition to this substance, a phenol-like compound, $C_6H_2Pr(OMe)_2{\cdot}OH$, is formed, and can be obtained from the alkaline filtrate by evaporating the alcohol and extracting the residue with ether. It forms a rather thick, yellowish liquid, boiling at 277—278° under atmospheric pressure, and at 168° under 36 mm. It is soluble in aqueous alkalis, but not in solutions of alkaline carbonates. It dissolves slightly in warm water, and the solution gives a brown precipitate with ferric chloride. When heated with methyl iodide and potash, the hydroxyl is converted into methoxyl, but some secondary changes also occur.

By the action of bromine on isoapiole, Ginsberg obtained a tribromisoapiole; when this is boiled in alcoholic solution with zinc-dust, *monobromisoapiole*, $C_{12}H_{13}BrO_4$, is formed. This crystallises from alcohol in needles, melts at 51°, and dissolves in alcohol and ether, but not in water, and with concentrated sulphuric acid gives a brown solution. *Isoapiole dibromide*, $CH_2{:}O_2{:}C_6H(OMe)_2{\cdot}C_3H_5Br_2$, can be obtained by treating a cooled ethereal solution of isoapiole with bromine until a yellow colour appears. It crystallises from light petroleum in rhombic plates which melt at 75°, and are decomposed when boiled with water or alcohol, hydrobromic acid being formed. When treated with zinc-dust in alcoholic solution, an oily product, apparently different from isoapiole, is obtained. Ginsberg's tribromisoapiole is probably the dibromide of monobromisoapiole.

Apionol must have the formula $C_6H_2(OH)_4$ [(OH_4) = 1 : 2 : 3 : 4], because it is a tetrahydroxybenzene, and is different from the symmetrical 1 : 2 : 4 : 5-tetrahydroxybenzene of Nietzki and Schmidt, and its tetramethyl-derivative is different from the 1 : 3 : 4 : 5-tetramethoxybenzene described by Will. In confirmation of this, the authors have shown that the dinitroapione obtained by nitrating apione has the nitro-groups in the ortho-positions, for the diamido-compound which it yields when reduced reacts readily with ortho-diketones forming azines. *Dinitroapione*, $C_9H_8N_2O_8$, obtained by pouring an acetic acid solution of apione into cooled nitric acid and diluting the solution with water, crystallises from alcohol in brilliant, yellow needles melting at 117—118°. By reducing it with tin and hydrochloric acid, adding excess of potash, and extracting with ether, *diamidoapione*, $C_9H_{12}N_2O_4$, was obtained; it crystallises from ether in faintly yellowish prisms melting at 119°, and dissolving in water to a yellow solution; this reduces gold and platinum chlorides, gives a green and then a reddish-brown colour with ferric chloride, and itself decomposes with deepening of colour when heated. The *hydrochloride* forms colourless, the *picrate*, yellow needles. With acetic anhydride, it yields *tetracetyldiamidoapione*, $C_9H_8O_4(NAc_2)_2$, which crystallises from alcohol in colourless needles melting at 133°. When treated with diacetyl and with benzile, azines are obtained, which have respectively the formulæ $C_9H_8O_4{<}\begin{matrix}N-CMe\\ | \quad\ \ \| \\ N-CMe\end{matrix}$ and $C_9H_8O_4{<}\begin{matrix}N-CPh\\ | \quad\ \ \| \\ N-CPh\end{matrix}$, and the melting points 176° and 222°. They both crystallise in yellow needles, and the latter gives a deep violet-red coloration with strong sulphuric acid. *Dinitrotetramethylapionol*, $C_6(OMe)_4(NO_2)_2$, obtained by pouring an acetic acid solution of tetramethylapionol into cooled nitric acid, and diluting with water, crystallises from alcohol in yellow crystals melting at 92°, soluble in alcohol, ether, and acetic acid, insoluble in water and alkalis.

Apionol having the formula given above, apione must have one of the two formulæ $C_6H_2(OMe)_2{<}^{O}_{O}{>}CH_2$ = [$(OMe)_2$: (O_2CH_2) = 1 : 2 : 3 : 4; or 1 : 4 : 2 : 3].

Having regard to the above formula of apionol, and to the analogy between apiole and safrole, it is evident that apiole must have one of the two formulæ $C_6H(C_3H_5)(OMe)_2{<}^{O}_{O}{>}CH_2$

[C_3H_5 : $(OMe)_2$: (O_2CH_2) = 1 : 2 : 3 : 4 : 5; or 1 : 2 : 5 : 3 : 4].

And, as in the reduction of isoafrole (this vol., p. 966), the oxygen in the para-position to the allyl-group is the one which is lost; hence the phenol-compound obtained by reducing isoapiole has one of the two formulæ $C_6H_2(C_3H_7)(OMe)_2 \cdot OH$ [C_3H_7 : $(OMe)_2$: OH = 1 : 2 : 3 : 5; or 1 : 2 : 5 : 3]. The corresponding trimethoxy-compound can only have one formula [C_3H_7 : $(OMe)_3$ = 1 : 2 : 3 : 5]; it is not, however, identical with the compound obtained by reducing Will's asarone, $C_6H_2(C_3H_5)(OMe)_3$, probably = 1 : 2 : 4 : 5.

The C_3H_5-group in apiole is probably allyl; in isoapiole, propenyl; and this is the cause of the isomerism of these two substances.

C. F. B.

Trimethylphenylmethane. By M. SEŃKOWSKI (*Ber.*, **23**, 2412—2420).—Trimethylphenylmethane has previously been obtained; it is best prepared by treating benzene (3 parts) with isobutyl chloride (1 part) and aluminium chloride (1 part) for two days, the temperature never being allowed to exceed 4°. The product is poured into a mixture of ice and water and distilled in a current of steam, the distillate is washed, fractionated, and the portion boiling at 167—168° treated with bromine in direct sunlight; after further washing, the product is finally distilled over sodium. The pure hydrocarbon boils at 167—167·5°; the yield is 70 per cent. of the theory. Trimethylphenylmethane dissolves in excess of nitric acid, and on pouring the product into water and fractionating the oil which separates, two isomeric nitro-compounds are obtained; they are probably ortho- and para-derivatives, although there is no direct proof. *Orthonitrophenyltrimethylmethane*, $CMe_3{\cdot}C_6H_4{\cdot}NO_2$, is a yellow, viscid liquid, of sp. gr. 1·074 at 15°; it boils at 247·4—248·4° under a pressure of 737·8 mm., and is miscible with ether, alcohol, or benzene. *Orthamidophenyltrimethylmethane*, $CMe_3{\cdot}C_6H_4{\cdot}NH_2$, is obtained by the reduction of the nitro-compound with tin and hydrochloric acid; it is a colourless, oily, strongly refractive liquid, of sp. gr. 0·9769 at 15°; it boils at 233—235°, and becomes coloured on exposure to air. The *sulphate* is sparingly soluble in water, from which it crystallises in plates. The *hydrochloride* is deposited in small needles. The *nitrate* crystallises in needles, and dissolves most readily in water. The *platinochloride* is obtained as an insoluble, yellow, crystalline precipitate. All these salts remain unchanged on exposure to air. The *acetyl-derivative*, $CMe_3{\cdot}C_6H_4.NHAc$, crystallises from benzene in radiating groups of long needles melting at 159°.

Paranitrophenyltrimethylmethane crystallises from alcohol in yellow needles melting at 30°, and boiling at 274·6—275° under a pressure of 737·8 mm. *Paramidophenyltrimethylmethane* resembles the ortho-compound; it boils at 239·4—240·4° under a pressure of 739·2 mm., and has a sp. gr. of 0·9525 at 15°. The *sulphate* crystallises from water in long, colourless, lustrous needles; the *nitrate* is readily soluble; the *hydrochloride* and *platinochloride* crystallise from water in needles. The *acetyl-derivative* is deposited from benzene in long, flat needles melting at 172°. Both the ortho- and para-amines give a yellow colour with ferric chloride.

Paratertiarybutylbenzenesulphonic acid, $CMe_3{\cdot}C_6H_4{\cdot}SO_3H$, is prepared by treating the hydrocarbon with fuming sulphuric acid at ordinary temperatures; it is a very hygroscopic, white, crystalline powder, melting at 62—63°; it appears to be the only sulphonation-product. The *potassium salt*, $CMe_3{\cdot}C_6H_4{\cdot}SO_3K + H_2O$, is sparingly soluble in cold water, and crystallises in plates. The *calcium salt*, $(C_{10}H_{13}{\cdot}SO_3)_2Ca + 4H_2O$, is deposited from water in plates. *Paratertiarybutylphenol*, $CMe_3{\cdot}C_6H_4{\cdot}OH$, is prepared by fusing the potassium sulphonate with potassium hydroxide; it may also be obtained from the amido-derivative by means of the diazo-reaction. It is a white,

crystalline powder, melting at 98·5°, and boiling at 238—239° under a pressure of 737 mm.; it sublimes at about 100°, and forms long needles, readily soluble in alcohol, ether, and alkalis; it has an odour resembling that of Russian leather. The *methoxy-derivative*, $CMe_3{\cdot}C_6H_4{\cdot}OMe$, is obtained by the action of methyl iodide on the potassium phenoxide: it is a colourless liquid of sp. gr. 0·9439 at 15°, and boils at 221·4—222·4° under a pressure of 730·5 mm. The *ethoxy-derivative*, $CMe_3{\cdot}C_6H_4{\cdot}OEt$, closely resembles the preceding compound; it boils at 233—233·6° under a pressure of 730·5 mm., and has a sp. gr. of 0·9331 at 15°.

Tertiary dibutylbenzene, $C_6H_4(CMe_3)_2$, is separated from the higher-boiling fractions obtained during the purification of tertiary butylbenzene; it is readily soluble in alcohol, and is deposited in long crystals melting at 70°, and boiling at 235—235·5° under a pressure of 736·5 mm.

Tertiary tributylbenzene, $C_6H_3(CMe_3)_3$, is formed together with the previous compound; it crystallises from alcohol in scales melting at 128°, and boiling at 291—292° under a pressure of 736·6 mm. A liquid hydrocarbon boiling about 227—230° is also formed in small quantity.
J. B. T.

Carbazoledisulphonic Acid. By J. BECHHOLD (*Ber.*, **23**, 2144—2146).—Pure carbazoledisulphonic acid, $C_{12}H_7N(SO_3H)_2$, can be prepared in the following manner:—Carbazole is warmed for a short time with sulphuric acid of sp. gr. 1·84, the product poured into water, the solution neutralised with barium carbonate and evaporated. The mixture of barium mono- and di-sulphonate obtained in this way is purified by repeatedly dissolving it in water and reprecipitating with alcohol, but it cannot be obtained in crystals; on decomposition with sulphuric acid, it yields the free acids in the form of a gelatinous precipitate, which is almost insoluble in alcohol, but soluble in water. When the crude acid mixture is dissolved in water, and a 3 per cent. solution of potassium permanganate gradually added until a permanent coloration is produced, all impurities are destroyed, and the filtered solution, on evaporation, yields the salt $C_{12}H_7N(SO_3K)_2$ in yellowish crystals. The free disulphonic acid, prepared by decomposing a concentrated solution of the potassium salt with hydrofluosilicic acid, adding a little alcohol, and evaporating the filtered solution, crystallises in colourless needles, and decomposes at a high temperature, but without melting. When the potassium salt is heated with concentrated hydrochloric acid at 200°, it yields pure carbazole.
F. S. K.

Benzidine. By H. SCHIFF and A. VANNI (*Chem. Centr.*, 1890, i, 941—942; from *L'Orosi*, **13**, 1).—By the action of diethylbenzidine (1 mol.) and phthalic anhydride (1 mol.), *phthalyldiethylbenzidine*, $C_6H_4{<}\begin{matrix}CO{\cdot}NEt{\cdot}C_6H_4\\ | \\ CO{\cdot}NEt{\cdot}C_6H_4\end{matrix}$, is obtained. It forms small, yellow crystals which melt at 250° with decomposition. It is slightly soluble in cold alcohol, but almost insoluble in water, ether, and chloroform, or in cold acids, or caustic alkalis. If allowed to remain with alcoholic potash for

some time at ordinary temperatures, *potassium diethylbenzidinephthalate* is formed, from which the free acid may be obtained by the action of hydrochloric acid; it is, however, not very stable.

Tetrethylbenzidine (1 mol.) and phthalic anhydride (2 mols.) combine together directly to form *tetrethylbenzidinephthalic acid*, $C_{36}H_{36}N_2O_6$. It is a white powder, readily soluble in alcohol and chloroform, insoluble in water, ether, and light petroleum. If the alcoholic solution is boiled for a short time, or if it is treated with alkalis in the cold, decomposition sets in. Hydroxylamine and phenylhydrazine do not react with it.

Ethyl chlorocarbonate reacts with benzidine, forming *benzidinediurethane*, $COOEt\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot COOEt$, which melts at 230°. It forms colourless needles, insoluble in water, sparingly soluble in ether and light petroleum, readily in boiling alcohol. Alcoholic ammonia partially converts it into benzidinesemiurethane. By boiling it with aniline, it is converted into benzidine, alcohol, and diphenylcarbamide; by boiling it with pure benzidine, it forms benzidine, alcohol, and probably a polymeride of benzidinecarbamide. These reactions do not take place in alcoholic solution.

When benzidine (2 mols.) and ethyl chlorocarbonate (2 mols.) react, benzidinediurethane, benzidine hydrochloride, and a considerable quantity of *benzidinesemiurethane hydrochloride*

$$COOEt\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH_2,HCl,$$

are formed. The free urethane is obtained from the hydrochloride by treatment with sodium carbonate. It is an amorphous, grey powder, melting at 90°, readily soluble in alcohol, sparingly in boiling water. The acetate dissolves in acetic acid, alcohol, and light petroleum, but is almost insoluble in water and ether. With salicylaldehyde, it forms the compound

$$COOEt\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot N{:}CH\cdot C_6H_4\cdot OH,$$

readily soluble in light petroleum, sparingly in ether; it melts at 170°. It is insoluble in potassium hydroxide; it gives no reaction with ferric chloride. With glyoxal, it forms the compound

$$COOEt\cdot NH\cdot C_{12}H_8\cdot NH\cdot CH(OH)\cdot CH(OH)\cdot NH\cdot C_{12}H_8\cdot NH\cdot COOEt.$$

This is a yellow powder, which is soluble in alcohol, and decomposes on exposure to the air. The following condensation-products are obtained with benzidine and aldehydes. *Salicylbenzidine*, $C_{12}H_8N_2(C_7H_5\cdot OH)_2$, crystallises from boiling benzene in lustrous, colourless needles, which melt at 264°; they become yellowish when exposed to the air. *Metanitrobenzylidenebenzidine*, $C_{12}H_8N_2(C_7H_5\cdot NO_2)_2$, separates from boiling benzene in small, orange-yellow crystals, sparingly soluble in water, and melting at 234°. *Cumylidenebenzidine*, $C_{12}H_8N_2(C_{10}H_{12})_2$, forms lustrous plates, which melt at 268°. Acetaldehyde forms a compound which may be considered as *amidophenylenequinaldine*,

$$NH_2\cdot C_6H_4\cdot C_6H_3<\begin{matrix}N{=}CMe\\ \vert\\ CH{:}CH\end{matrix} + \tfrac{1}{2}H_2O.$$

It is a white powder, nearly insoluble in the usual solvents, sparingly

soluble in chloroform. *Isobutylenebenzidine*, $C_{12}H_8N_2(C_4H_8)_2$, readily soluble in light petroleum, melts at 230° with decomposition. *Œnanthylidenebenzidine*, $C_{12}H_8N_2(C_7H_{14})_2$, forms small, white crystals melting at 112—115°, and readily soluble in light petroleum.

Tolidine forms analogous compounds with aldehydes; *cumylidenetolidine*, $C_{12}H_6Me_2N_2(C_{10}H_{12})_2$, crystallises from a mixture of alcohol and light petroleum in needles; it melts at 152°. *Cinnamylidenetolidine*, $C_{12}H_6Me_2N_2(C_9H_8)_2$, crystallises from light petroleum; it melts at 213—214°. *Furotolidine*, $C_{12}H_6Me_2N_2(C_5H_4O)_2$, crystallises from light petroleum in lustrous, gold plates; it melts at 192°. The author finds that benzidine is sparingly soluble in boiling water, 1 part dissolving in 106·5 parts. J. W. L.

Isomerism in the Stilbene-group. By P. WALDEN and A. KERNBAUM (*Ber.*, **23**, 1958—1961).—It has been shown by Bisehoff (Abstr., 1888, 1094) that orthonitrostilbene forms two isomerides, corresponding with fumaric and maleïc acids. The authors find that paranitrostilbene, obtained by the action of alcoholic potash on paranitrobenzyl chloride, also forms two geometrical isomerides. The one crystallises in pale-yellow needles which melt at 280—285°, and are readily soluble in hot acetic acid, aniline, acetone, and ethylene bromide, sparingly in alcohol, ether, chloroform, and benzene. The second isomeride crystallises in reddish-yellow needles melting at 210—216°, and is less soluble than the first compound in ether and alcohol, but dissolves more readily in acetone, benzene, and chloroform. H. G. C.

Contributions to the Theory of Six-membered "Rings." By E. BAMBERGER (*Annalen*, **257**, 1—55).—The investigations of the author and his pupils on the reduction of the amines and phenols of naphthalene in boiling amyl alcohol solution by means of sodium (Abstr., 1888, 159, 599, 712, 959; 1889, 715, 717, 737, 782, 888, 891, 892, 1000, 1198; this vol., pp. 506, 508, 627, 631) show that in every case four atoms of hydrogen are taken up asymmetrically, that is, are added on to one of the rings and not distributed between the two. The effect of reduction on the properties of the substance depends entirely on the distribution of the added hydrogen-atoms: "alicyclic" derivatives, which contain both the substituent and the added hydrogen-atoms in the same nucleus, react like fatty amines or alcohols, whilst "aromatic" derivatives, which contain the substituent in one and the added hydrogen atoms in the second nucleus, exhibit the aromatic characters of the parent substances, but in a more marked degree, the properties of ar.-tetrahydro-α-naphthylamine, for example, approximating more to those of aniline than to those of α-naphthylamine.

Dealing with "aromatic" tetrahydro-compounds, the author cites the following evidence to prove that the peculiar properties which distinguish derivatives of naphthalene from those of benzene disappear on hydrogenation. An aqueous solution of 1:4-naphthylenediamine sulphate to which sodium acetate and aniline hydrochloride have been added, becomes reddish-brown on treatment with potassium dichromate,

and gives a dirty brown, flocculent precipitate. ar.-Tetrahydro-1 : 4-naphthylenediamine, when oxidised under similar conditions, behaves like paraphenylenediamine in forming an indamine and a saffranine. *Tetrahydronaphthindamine* is precipitated in glistening, bronze-green crystals on the addition of salt to its green aqueous solution, and exhibits all the characters of an indamine; when boiled with dilute acid, it decomposes into tetrahydro-α-naphthaquinone, which is volatile with steam, and is readily recognised by its pungent odour. Again, an acidified solution of 1 : 4-naphthylenediamine containing hydrogen sulphide, when treated with ferric chloride, gives a dull, dark-brown, flocculent precipitate, the liquid becoming yellowish-brown. ar.-Tetrahydro-1 : 4-naphthylenediamine, on the contrary, behaves like paraphenylenediamine under these conditions, and is converted into a thionine. *Tetrahydronaphthathionine* crystallises in lustrous, slender, dark-violet needles showing a metallic lustre, and readily dyes silk and wool producing a dark-violet shade. Further, the dichlorodiimides of 1 : 4-naphthylenediamine and paraphenylenediamine differ in the colours they give with aromatic bases, and comparison shows that the colours obtained with tetrahydro-1 : 4-naphthylenedichlorodiimide under similar conditions resemble those from the latter rather than those from the former. *ar.-Tetrahydro-1 : 4-naphthylenedichlorodiimide*, $C_{10}H_{10}(NCl)_2$, crystallises from ether in long, silky, yellowish-white needles, melts at 68°, is sparingly soluble in water, but readily in the usual organic solvents, and gives a violet colour when warmed with an alcoholic aniline solution and hydrochloric acid, and an emerald-green with dimethylaniline.

As evidence that naphthalene compounds on conversion into "aromatic" tetrahydro-derivatives lose their specific naphthalene characters, the author adduces the following examples amongst others. The naphthols yield alkyl-derivatives when heated at 150° with alcohol and hydrochloric acid (Liebermann and Hagen, Abstr., 1882, 1212), but the "aromatic" tetrahydronaphthols, like phenol and most of its homologues, are not acted on under similar conditions. The naphthols can readily be converted into naphthyl sulphates (Nietzki, Abstr., 1882, 736), but the "aromatic" tetrahydronaphthols resemble phenol in not forming sulphates. α- and β-Naphthaquinone react with phenylhydrazine forming hydrazones (Zincke, *Ber.*, **18**, 786, footnote), but ar.-tetrahydro-α-naphthaquinone, under like conditions, is reduced to ar.-tetrahydro-α-naphthaquinol, the resemblance to ordinary quinone being further marked by the close similarity in crystalline character, volatility, colour, odour, &c.

The alteration in properties involved in the reduction of naphthalene-derivatives to "aromatic" tetrahydro-bases is strikingly shown by the marked resemblance in properties of ar.-tetrahydro-α-naphthylamine to 1 : 2 : 3-orthoxylidine, and of ar.-tetrahydro-α-naphthol to 1 : 2 : 3-orthoxylenol.

With reference to "alicyclic" reduction, it is already known that "alicyclic" tetrahydro-derivatives have all the characters of fatty amines or alcohols; the author, in this connection, points out that the properties of ac.-tetrahydro-β-naphthylamine and ac.-tetrahydro-β-naphthol are identical with those which β-amido- or β-hydroxy-

orthodiethylbenzene would be expected to have, and further shows that ac.-tetrahydro-β-naphthylamine closely resembles the known phenylethylamine in properties, the similarity being especially marked in the case of the nitrites of the two compounds, which can be crystallised from boiling water, and when decomposed are converted, with elimination of ammonia, into unsaturated hydrocarbons, the former yielding dihydronaphthalene (Bamberger and Müller, Abstr., 1888, 712), the latter cinnamene (Fileti and Piccini, Abstr., 1879, 922).

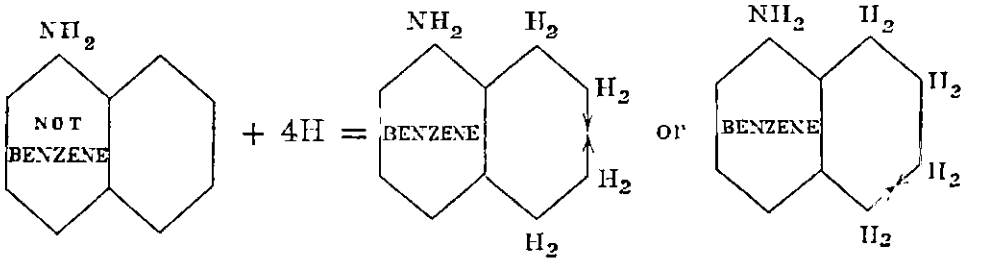
The consideration of these points leads to the deduction of the following laws:—

I. In naphthalene, and those of its derivatives in which each of the eight carbon atoms is united with a monad radicle, two carbon systems are present, neither of which exists as a benzene-ring, but is converted into one when the second takes up four atoms of hydrogen.

II. The effect of the addition of four atoms of hydrogen to either of the two carbon systems of naphthalene and its derivatives is to cause that system to assume the properties of an open (fatty) chain.

III. Tetrahydrogenation in the naphthalene series results in the product reacting as if it were a benzene-derivative with a fatty side-chain. The hydrogenated system assumes the fatty, and the non-hydrogenated the benzene functions.

Graphically, the reduction of α-naphthylamine can be represented as follows, the chain with arrow-heads indicating a ring with fatty functions:—

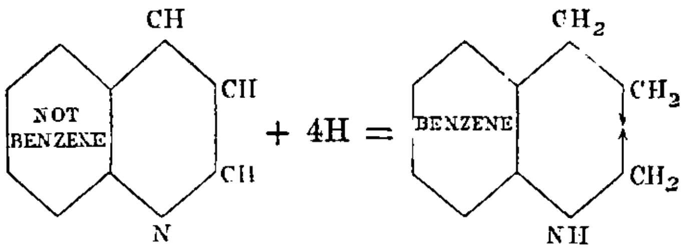


In connection with the first law, the author discusses the various formulæ hitherto proposed for naphthalene, and discards them as inadequate, since they all fail to give expression to the view that a ring system which is *similar* to benzene becomes *identical* with it by reduction.

As an investigation of naphthalene-derivatives with the object of accumulating experimental evidence of the change in the character of the rings could hardly lead to any satisfactory result, the author has employed a compound with dissimilar rings, choosing quinoline for this purpose—the assumption being made that the atomic arrangement and distribution of valency corresponds exactly in quinoline and naphthalene.

On reduction, quinoline exhibits the properties of an alkylated

aniline, the pyridine ring which takes up the four hydrogen-atoms assuming the character of a side-chain:—



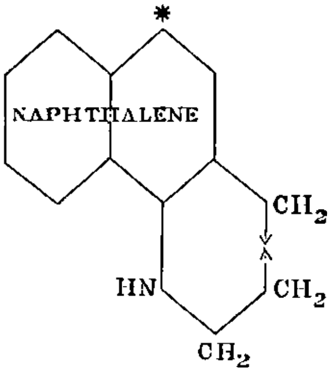
Quinoline. Tetrahydroquinoline.

As evidence of this change in properties, the author quotes the resemblance of kairoline (1'-methyltetrahydroquinoline) to dimethylaniline (Feer and Koenigs, *Ber.*, **18**, 2389), the intramolecular change of the nitrosamine of tetrahydroquinoline into 3-nitrosotetrahydroquinoline (Ziegler, Abstr., 1888, 609), and the fact that tetrahydroquinoline, unlike quinoline but like dimethylaniline, forms a condensation compound with benzaldehyde analogous to leuco-malachite-green (Einhorn, *Ber.*, **19**, 1243). Further, the action of diazobenzenesulphonic acid on tetrahydroquinoline forms *sulphophenylazotetrahydroquinoline*, $C_{15}H_{15}N_3SO_3$, which crystallises in dark steel-blue needles with a metallic lustre, dissolves in aqueous soda with a dark-red colour, and, on reduction with stannous chloride, is converted into Ziegler's 3-amidotetrahydroquinoline (*loc. cit.*). Tetrahydroisoquinoline, as anticipated, does not form azo-dyes under these conditions, and closely resembles benzylamine in its properties.

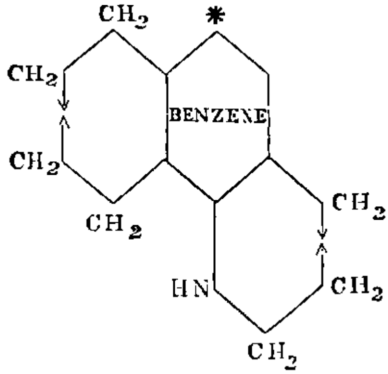
Substituted quinolines behave as quinoline does on reduction. Ziegler's 3-amidotetrahydroquinoline, unlike 3-amidoquinoline, exhibits the characters of a true phenylenediamine; thus, it gives the indamine and saffranine reactions when oxidised in the presence of aniline hydrochloride, forms dyes of the character of tolylene-blue and tolylene-red when treated with metaphenylenediamine and potassium dichromate, of the character of indoanilines with phenols and potassium dichromate, and of methylene-blue with hydrogen sulphide and ferric chloride. 2- and 4-hydroxyquinoline do not give dyes when heated with phthalic anhydride and zinc chloride, but their tetrahydro-derivatives, like metamidophenol, are converted under these conditions into *rhodamines*, which closely resemble ordinary rhodamine in properties, except that they produce less blue shades on silk and wool. It is further pointed out that the conversion of the methiodide of 1-hydroxykairoline (1-hydroxytetrahydro-1'-methylquinoline) into 1-methoxykairoline by treatment with caustic alkali (Fischer and Kohn, *Ber.*, **19**, 1040; Kohn, Trans., 1886, 501) corresponds with the conversion of the methiodide of dimethylorthamidophenol into methoxydimethylorthamidobenzene under similar conditions (Griess, Abstr., 1880, 637), since the "ring" containing the nitrogen-atom has only the configuration, and not the essential properties of a (pyridine) ring.

Naphthaquinolines, generally, do not react with diazo-compounds. Of the hydrogenated bases examined, py.-tetrahydro-α-naphtha-

quinoline, ar.-octohydro-α-naphthaquinoline, ar.-octohydro-β-naphthaquinoline, and ar.-octohydro-β-quinaldine give azo-colours, whilst py.-tetrahydro-β-naphthaquinoline, py.-tetrahydro-β-naphthaquinaldine, ac.-octohydro-β-naphthaquinoline, ac.-octohydro-β-naphthaquinaldine, and di-β-tetrahydro-α-naphthaquinoline do not. Inspection of the formulæ gives the explanation of these differences, when the conditions attending the formation of azo-dyes in the benzene and naphthalene series are borne in mind. Thus, for example, with the α-compounds:—

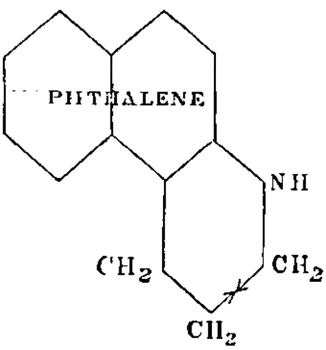


py.-Tetrahydro-α-naphthaquinoline.

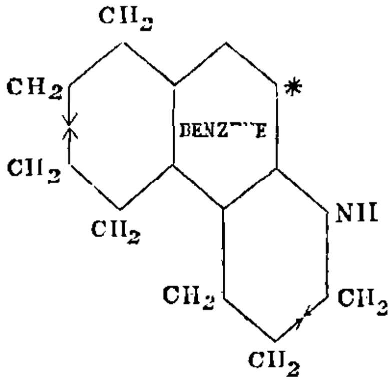


ar.-Octohydro-α-naphthaquinoline.

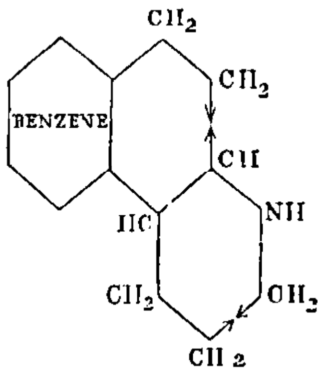
py.-Tetrahydro-α-naphthaquinoline behaves like an alkylated α-naphthylamine, and ar.-octohydro-α-naphthaquinoline like an alkylated aniline, the azo-group taking up the para-position to the nitrogen atom. With the β-compounds—



py.-Tetrahydro-β-naphthaquinoline.



ar.-Octohydro-β-naphthaquinoline.

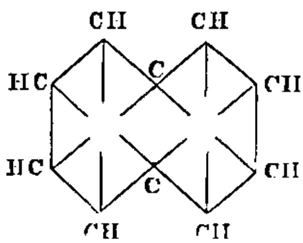


ac.-Octohydro-β-naphthaquinoline.

py.-Tetrahydro-β-naphthaquinoline reacts as an alkylated β-naphthylamine but cannot form colours since the contiguous α-position is occupied; ar.-octohydro-β-naphthaquinoline behaves like an alkylated aniline, and the para-position to the nitrogen-atom being closed, forms an ortho-azo-dye, whilst ac.-octohydro-β-naphthaquinoline

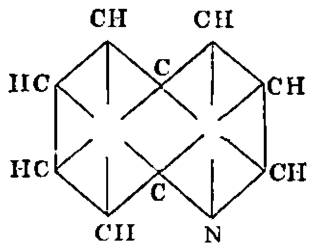
reacts as an alkylated benzylamine, and does not give azo-dyes but diazoamido-derivatives by the action of diazo-compounds.

Returning to the discussion of naphthalene formulæ, it is pointed out that the Claus formula is based on the supposed asymmetry of the naphthalene molecule (*Ber.*, **9**, 590, 1606; **10**, 1303). No valid evidence of this asymmetry has been adduced, and as a further argument for the symmetry of the molecule, the author shows that 2 : 2′-dihydroxynaphthalene, like β-naphthol, is readily etherified by digestion with alcohol and sulphuric acid on a water-bath. From a consideration of the three laws already quoted (*v. supra*) and the symmetry of the molecule, the author is led to extend Armstrong's and v. Baeyer's conception of the benzene molecule (Trans., 1887, 264; *Annalen*, **245**, 128) to naphthalene, and to assign to the latter the symbol—



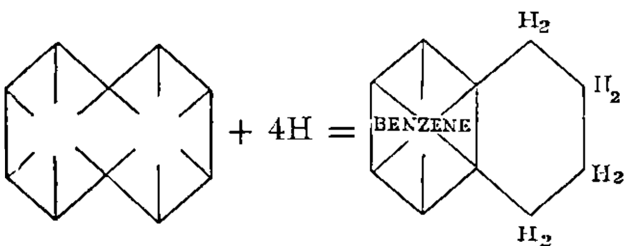
Naphthalene.

whence



Quinoline.

Such a symbol represents naphthalene as composed of two similar carbon-systems, neither of which is identical with, although similar to, a benzene ring. The effect of hydrogenation on the molecule, and conversion of one of the systems into a ring identical with that of benzene, is represented by the graphic equation—



The remainder of the paper is devoted to a discussion of this formula, and the extension of the conception to more complex ring-compounds, such as anthracene and phenanthrene. W. P. W.

Characteristics of the Hydrogenation Process. By E. Bamberger and F. Lengfeld (*Ber.*, **23**, 1124—1137).—ar.-Tetrahydro-α-naphthol does not give a trace of tetrahydronaphthyl sulphate when treated with concentrated sulphuric acid in the cold, of tetrahydronaphthyl ethyl ether when heated with an equal weight of 39 per cent. hydrochloric acid and three times its weight of absolute alcohol for 7—8 hours at 150°, or of dinaphthyl ether when boiled with $2\frac{1}{2}$ times its weight of dilute sulphuric acid (1 : 1), and differs there-

fore from α-naphthol in all these reactions. With sodium nitrite and concentrated sulphuric acid, it gives a brownish-red colour, which, after the addition of water and caustic soda, becomes yellowish-green, whilst it gives no colour reaction either with bleaching powder or with ferric chloride, thus resembling 1 : 2 : 3-orthoxylenol.

ar.-Tetrahydro-β-naphthol is not etherified by heating with concentrated sulphuric acid and absolute alcohol on a water-bath for seven hours, and does not form a trace of tetrahydronaphthyl sulphate when treated with concentrated sulphuric acid in the cold.

ar.-Tetrahydro-α-naphthaquinone, $C_{10}H_{10}O_2$, can be prepared from ar.-tetrahydro-α-naphthylamine by oxidation with sodium dichromate and dilute sulphuric acid on the lines of Nietzki's quinone-process, the yield amounting to 20 per cent. of the theoretical. It closely resembles quinone in odour, volatility, colour, lustre, solubility, crystalline character, &c.; melts at 55·5° (that is, within half a degree of orthoxyloquinone), and is reduced to ar.-tetrahydro-α-naphthaquinol by treatment with phenylhydrazine.

ar.-Tetrahydro-α-naphthaquinol, $C_{10}H_{10}(OH)_2$, may be obtained by digesting ar.-tetrahydro-α-naphthaquinone for 48 hours with sulphurous acid at the ordinary temperature of the air, boiling the colourless aqueous solution for a few minutes, and finally extracting with ether. It closely resembles quinol in properties, crystallises in aggregates of slender, colourless prisms, sublimes without decomposition in beautiful needles, melts at 172—172·5°, and is soluble in the ordinary organic solvents and in hot water. By careful oxidation with potassium dichromate in the cold, it can be converted into the *quinhydrone*; further oxidation results in the formation of ar.-tetrahydro-α-naphthaquinone.

ar.-Tetrahydro-α-naphthylamine resembles α-naphthylamine rather than aniline in forming an amidoazo- instead of a diazoamido-compound on treatment with diazo-compounds. *ar.-Amidoazotetrahydro-α-naphthalene*, $C_{10}H_{11}\cdot N_2\cdot C_{10}H_{10}\cdot NH_2$, is obtained by the action of amyl nitrite (1 mol. prop.) on the tetrahydro-base (2 mol. props.), or by diazotising a mixture of the tetrahydro-base (1 mol. prop.) and its hydrochloride (1 mol. prop.) with sodium nitrite (1 mol. prop.). It crystallises from alcohol in orange-red, lustrous needles, melts at 141°, and is readily soluble in benzene, chloroform, ether, light petroleum and boiling alcohol, insoluble in water. W. P. W.

Action of Sulphurous Anhydride on Nitroso-compounds. By M. Schmidt (*J. pr. Chem.* [2], **42**, 156—157).—Acetone and amidosulphonic acid are produced when sulphurous anhydride acts on acetoxime, CMe_2:NOH, in aqueous solution.

α-Nitroso-β-naphthol and β-nitroso-α-naphthol both give amidosulphonic acids when sulphurous anhydride is passed into their alcoholic solutions or when they are dissolved in sodium hydrogen sulphite and the solution decomposed by hydrochloric acid; but α-nitroso-α'-naphthol does not give a similar result.

The amidonaphtholsulphonic acid from α-nitroso-β-naphthol crystallises in colourless needles (with $\frac{1}{2}$ mol. H_2O), which gradually become red; it is insoluble in the usual solvents, but dissolves in

sodium acetate and hot sodium hydrogen sulphite solutions; the latter solution has a blue fluorescence. The acid is easily oxidised, reducing ammoniacal silver solutions.

The amidosulphonic acid from β-nitroso-α-naphthol crystallises in stellate groups of needles (with $1\frac{1}{2}$ mols. H_2O); in properties it resembles the other acid. A. G. B.

αα-Dithionaphthol. By L. GROSJEAN (*Ber.*, **23**, 2370—2371; compare Abstr., 1889, 715).—*αα*-Dithionaphthol, $C_{10}H_6(SH)_2$, is prepared by treating sodium αα-naphthylenedisulphonate (10 parts) with phosphorus pentachloride (14 parts), and pouring the product into a mixture of 210 parts of dilute sulphuric acid (1 : 2·5) and 35 parts of zinc-dust. When the reduction is completed, the insoluble portion is separated, washed, dried, and extracted with ether. After evaporation of the ether, the residue is purified by distillation, and crystallisation from alcohol, from which it is deposited in lustrous plates melting at 180—181°, and boiling at 210° under a pressure of 15 mm. The compound is very sparingly soluble in ether, light petroleum, or toluene; the alcoholic solution gives a deep-yellow precipitate with lead acetate; in the dry state it is not acted on by air, but in alkaline solution it readily oxidises with formation of a white powder soluble in aniline; on adding hydrochloric acid, this is precipitated unchanged, and remains solid at 220°.

Benzoyldithionaphthol, $C_{10}H_6(SBz)_2$, is prepared by the action of benzoic chloride, and is deposited from alcohol in lustrous crystals melting at 152—153°. The *acetyl*-derivative, $C_{10}H_6(SAc)_2$, is obtained by means of acetic chloride; it separates from alcohol in colourless crystals melting at 110°. J. B. T.

Thio-derivatives of Aromatic Amines. By O. KYM (*Ber.*, **23**, 2458—2468; compare Abstr., 1889, 51).—*Benzoylthio-β-dinaphthylamine*, $S<^{C_{10}H_6}_{C_6H_{10}}>NBz$, is prepared by heating thio-β-dinaphthylamine with benzoic anhydride at 210°; the product is treated with aqueous sodium hydroxide, and purified by dissolving in benzene; on the addition of light petroleum or alcohol to this solution, it crystallises out in groups of almost colourless needles, melting at 196—197°. It dissolves sparingly in alcohol or ether, and is insoluble in light petroleum.

Methylthio-β-dinaphthylamine, $S<^{C_{10}H_6}_{C_{10}H_6}>NMe$, is obtained by heating thio-β-dinaphthylamine with methyl iodide and methyl alcohol at 150°; after repeated crystallisation from benzene, it is deposited in lemon-yellow plates, or slender needles, melting at 284—285°. It is readily soluble in toluene, but more sparingly in benzene and alcohol. With concentrated sulphuric acid, a violet colour is gradually produced, which instantaneously changes to deep blue on the addition of nitric acid. The same compound is also formed on heating sulphur with methyl-β-dinaphthylamine at 240°, or by treatment with a benzene solution of sulphur mono- or dichloride at ordinary temperatures. No dithio-derivative could be

isolated in these experiments. The methyl-β-dinaphthylamine employed melted constantly at 123—124°, instead of 139—140°, as given by Ris (compare Abstr., 1888, 57).

Ethylthio-β-dinaphthylamine, $S<^{C_{10}H_6}_{C_{10}H_6}>NEt$, is prepared from thio-$\beta$-dinaphthylamine by the action of ethyl iodide, and from ethyl-β-dinaphthylamine by the action of sulphur mono- and di-chlorides. It crystallises from benzene in small tufts of bright-yellow needles melting at 212—213°, and resembles the methyl-derivative in general properties.

Thiophenyl-α-naphthylamine, $S<^{C_{10}H_6}_{C_6H_4}>NH$, is obtained on heating phenyl-α-naphthylamine with sulphur at 240°; the product is treated with benzene, and on recrystallisation from alcohol, it is deposited in small, yellow, lustrous plates melting at 137—138°. It gives a deep blue colour with concentrated sulphuric acid, which changes to red on adding nitric acid.

By heating crude thiophenyl-α-naphthylamine with recently-reduced, finely-divided copper at 280° for three hours, *phenyl-α-naphthylcarbazole*, $\begin{matrix}C_{10}H_6\\|\\C_6H_4\end{matrix}>NH$, is formed; it crystallises from dilute alcohol in small, pale, yellowish-green, lustrous plates, melts at 225°, and is readily soluble in glacial acetic acid, benzene, or alcohol, but insoluble in light petroleum.

Thiophenyl-β-naphthylamine, $S<^{C_{10}H_6}_{C_6H_4}>NH$, is prepared from phenyl-β-naphthylamine and sulphur; it crystallises from dilute alcohol in tufts of lustrous, light-yellow needles, melting at 178°, and resembling the isomeric compound described above in general properties. With concentrated sulphuric acid, it gives a deep-blue colour, changing to deep-violet on the addition of nitric acid. No carbazole-derivative could be obtained, as the compound may be distilled over heated copper without undergoing any change.

Methylthiophenyl-β-naphthylamine, $S<^{C_{10}H_6}_{C_6H_4}>NMe$, is formed by the action of methyl iodide on thiophenyl-β-naphthylamine; it crystallises from a mixture of benzene and alcohol in groups of pale, yellowish-green needles, melting at 132—133°. With concentrated sulphuric acid, it gives a deep-blue colour which is not altered by nitric acid. J. B. T.

Cyanamines, a New Group of Dyes. By O. N. Witt (*Ber.*, **23**, 2247—2252). The dye called naphthol-violet, which was first prepared by the author and Meldola (Trans., 1881, 37) simultaneously, by treating nitrosodimethylaniline hydrochloride with β-naphthol, is a mixture of several compounds which have, however, one property in common, namely, that when viewed by artificial light they appear red. The magenta-red dye obtained by Nietzki and Otto (Abstr., 1888, 949) from β-naphthol and quinonedichlorimide seems to be homogeneous, and has probably the constitution assigned to it by him.

When the free bases of these two dyes are warmed, they become

insoluble in ether, and are finally converted into substances of quite different appearance; when redissolved in acids, these new compounds both give dyes which have a greenish-blue shade, even when viewed by artificial light. Other dyes of the same group as naphthol-violet, such as the violet obtained from methyldihydroxynaphthalene, show a like behaviour, and the reaction is probably a general one. The author gives the name "cyanamine" to this class of new dyes.

The *cyanamine*, $C_{26}H_{26}N_4O_2$, formed from Meldola's β-naphthol-violet is best obtained by heating the freshly-prepared dye with an alcoholic solution of calcium hydroxide for 1 to $1\frac{1}{2}$ hours. The crystalline base is separated by filtration, washed with alcohol and water consecutively, then extracted with boiling alcohol, the residue dissolved in dilute hydrochloric acid, and the base precipitated from the boiling solution by ammonia. It crystallises from chloroform in blackish-brown plates, and is insoluble, or almost insoluble, in most ordinary solvents except chloroform, its solution being of a reddish-violet shade. It dissolves in concentrated acids yielding brownish-orange, and in dilute acids yielding blue solutions. The *sulphate* separates from alcohol in shining green scales, the *hydrochloride*, $C_{26}H_{26}N_4OCl_2$, in plates or prisms of the same colour; both compounds are readily soluble in water, by which they are partially converted into violet basic salts. The base is oxidised by chromic acid to a new violet-blue dye, the base of which is orange-red, and dissolves in ether yielding a yellow, fluorescent solution.

The constitution of the cyanamine base is probably expressed by the formula—

$$NMe_2{\cdot}C_6H_4{\cdot}\overset{4}{N}\underset{1'}{\overset{O\ 2'}{\diagup\!\!\!\!\!\_\_\_\!\!\!\diagdown}}C_{10}H_5{\cdot}\overset{4'\,1}{N}\overset{C_6H_4\ 4}{\diagup\!\_\_\_\_\_\!\diagdown}NMe_2{\cdot}OH.$$

F. S. K.

Constitution of Diphenyl- and Phenylnaphthylamine-Blue. By A. Hausdörfer (*Ber.*, **23**, 1961—1966).—Diphenylamine-blue was prepared according to Schoop's method (*Zeit. angew. Chem.*, 1887, 215), by heating diphenylamine with oxalic acid at 130—132°, extracting the product with boiling water, heating with alcohol, and precipitating with hydrochloric acid. It forms a brownish-red powder, which is soluble in hot aniline and nitrobenzene, less so in hot acetone, acetic acid, and alcohol. It dissolves in alcoholic potash forming a brownish-red solution, from which the colouring matter is reprecipitated by acids. It also dissolves in sulphuric acid, and is reprecipitated by water in blue flocks. After recrystallisation from acetic acid, it gave numbers agreeing with the formula $CCl(C_6H_4{\cdot}NHPh)_3$. In support of this formula is the fact that it is readily converted into a leuco-base on reduction, which on oxidation with chloranil again forms the original colouring matter. Moreover it is identical with the blue obtained from pararosaniline, the so-called triphenylpararosaniline.

When phenyl-α-naphthylamine and oxalic acid are heated together in a similar manner, the corresponding phenyl-α-naphthylamine-blue, $CCl(C_6H_4{\cdot}NH{\cdot}C_{10}H_7)$ is formed. It is readily soluble in aniline, more sparingly in acetone, acetic acid, and alcohol, and separates according to the nature of the solvent and the concentration, as a bluish-violet

or dark brownish-red powder, and was once obtained from acetone in crystals having a bronze lustre. It is also readily converted into a leuco-base.

Carbazole-blue probably has a similar constitution, but it was not found possible to obtain this compound sufficiently pure for analysis.

H. G. C.

Derivatives of α- and β-Naphthylglycin. By C. A. Bischoff and A. Hausdörfer (*Ber.*, **23**, 2003—2009).—As already stated by Bischoff and Nastvogel, α-naphthylglycin cannot by simple heating be converted into α-dinaphthyl-αγ-diketopiperazine,

$$C_{10}H_7N{<}{CH_2\cdot CO \atop CO\cdot CH_2}{>}N\cdot C_{10}H_7,$$

(Abstr., 1889, 1015). The latter may, however, be obtained by heating a mixture of α-naphthylglycin and acetic anhydride in molecular proportion. It crystallises from a mixture of alcohol and acetic acid in lustrous plates melting at 275°, and is identical with the compound obtained by Abenins (this vol., p. 269) from chloracetonaphthalide. By the action of alkalis, the ring appears to be split, and the acid $C_{10}H_7\cdot NH\cdot CH_2\cdot CO\cdot N(C_{10}H_7)\cdot CH_2\cdot COOH$ formed.

α-Naphthylimidodiacetic acid, $C_{10}H_7\cdot N(CH_2\cdot COOH)_2$, is obtained by heating together α-naphthylglycin, monacetonaphthalide, and chloracetic acid, and crystallises from benzene with benzene of crystallisation, which is given off at 100°. Both the acid containing benzene and that dried at 100° melt at 133—133·5°. It is readily soluble in alcohol, chloroform, and acetic acid, sparingly in benzene and light petroleum. By the action of α-naphthylamine, it is converted into the *mono-* and *di-naphthalide* melting at 197—199° and 200—202° respectively.

β-Dinaphthyl-αγ-diketopiperazine is obtained, unlike the α-compound, by simply heating β-naphthylglycin in a current of hydrogen at 220°. It forms colourless, very lustrous plates, which only decompose above 360°, and are insoluble in the ordinary solvents. As with the α-compound, the ring appears to be split with alkalis. The same piperazine may be obtained by dissolving β-naphthylglycinnaphthalide in amyl alcohol, adding first the theoretical quantity of sodium, then the corresponding quantity of ethyl chloracetate, and boiling for several hours.

When β-naphthylamine, chloracetic acid, and sodium acetate are heated together, the chief product is the extremely stable β-naphthylamine salt of β-naphthylglycin, already described by Jolles (Abstr., 1889, 1199). If, however, β-naphthylglycin be neutralised with sodium carbonate in aqueous solution, and the requisite quantity of chloracetic acid, also in aqueous solution, gradually added with constant stirring, and the whole heated at 130—150°, *β-naphthylimidodiacetic acid*, $C_{10}H_7\cdot N(CH_2\cdot COOH)_2$, is formed. This separates as a white precipitate which decomposes at 182°, and is soluble in alkalis, alcohol, and acetone, sparingly in ether and chloroform, and insoluble in benzene and light petroleum.

H. G. C.

Derivatives of Lapachic Acid. By E. PATERNÒ and G. MINUNNI (*Gazz.*, **19**, 601—623).—Paternò (Abstr., 1883, 210) found that when the red solution of an alkaline lapachate is treated with zinc-dust it becomes bright yellow, and on precipitation with hydrochloric acid yields a compound crystallising in colourless needles, which rapidly absorb oxygen and pass into lapachic acid. The authors find that even when all the operations are conducted in an atmosphere of hydrogen, the componnd precipitated by hydrochloric acid, although white at first, rapidly darkens; the ethereal solution, moreover, on distillation yields a blackish oil, the aqueous extract of which deposits on cooling the unstable needles mentioned. The composition of this substance was determined by drying the original ethereal solution with calcium chloride, and acetylating it in a current of carbonic anhydride. The product is the triacetyl-derivative of a trihydroxyamylenenaphthalene, $C_{15}H_{13}(OAc)_3$; it crystallises from alcohol in long, colourless prisms, which melt at 139°, and are insoluble in water. It slowly dissolves in a dilute solution of potash, and hydrochloric acid reprecipitates lapachic acid from the solution.

Diacetylhydroisolapachone and Isolapachone.—When lapachic acid is heated with excess of sodium acetate and acetic anhydride, the diacetyl-derivative of an unstable quinol, $C_{15}H_{14}O(OAc)_2$, crystallises out in needles melting at 131—132°; on carefully hydrolysing this substance in a reducing atmosphere, and dissolving the product in ether, a colourless solution is obtained which rapidly oxidises on desiccation, and is converted into a quinone isomeric with lapachic acid and lapachone. The authors term this substance *isolapachone*. It crystallises in orange needles melting at 140—141°, and it may be reconverted into the preceding diacetyl-derivative by reduction and acetylation.

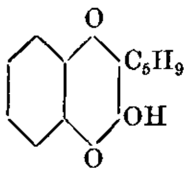
Diacetylhydrolapachone.—When an alcoholic solution of lapachone is reduced with an equal weight of sodium, and the precipitate formed by hydrochloric acid taken up with ether in a reducing atmosphere, the solution leaves on distillation a black oil which partly resinifies on standing; if the solution is directly acetylated, a diacetyl-derivative, $C_{15}H_{14}(OAc)_2$, is formed, which crystallises from alcohol in colourless cubes, melts at 161°, and is slightly soluble in cold alcohol, ether, &c.

Lapachic acid does not yield an oxime or hydrazone when treated by ordinary methods; an *oxime*, $C_{15}H_{14}O_2{:}NOH$, crystallising in greenish-yellow prisms may, however, be obtained by treating a cold alcoholic solution of lapachic acid with twice its weight of hydroxylamine hydrochloride and an equivalent quantity of sodium carbonate, the mixture being allowed to remain for three or four days. The *hydrazone*, $C_{15}H_{14}O_2{:}N_2PhH$, may be obtained by dissolving the acid directly in phenylhydrazine, heating to 120°, and allowing it to remain for a few days. It crystallises from alcohol in tufts of brick-red needles which melt at 108—109°, and are only slightly soluble in ordinary solvents.

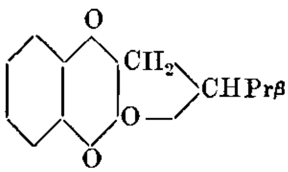
Lapachone readily forms a *monoxime*, which crystallises from alcohol in silky, orange-yellow, pointed prisms, and melts at 168·5—169·5°. The *benzoyl-derivative*, $C_{15}H_{14}O{:}NOBz$, forms golden-yellow plates, melting at 180—181°. On reducing the oxime with

tin and hydrochloric acid, the solution successively acquires a brown and a deep-violet colour, and contains lapachone together with a substance crystallising in yellow needles and melting at about 110°. The *hydrazone* forms orange-yellow needles, which melt at 188—189° and dissolve sparingly in alcohol, ether, or acetic acid, and moderately in benzene. On reducing an acetic acid solution with sodium amalgam, a blood-red solution is obtained, but no definite compound could be isolated.

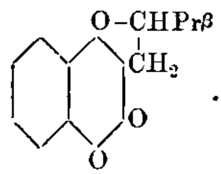
The substance obtained by Paternò in red crystals (blue by transmitted light) by treating lapachone with acetic anhydride and sodium acetate, has the composition $C_{30}H_{26}O_5$, and is probably an anhydride of lapachone or of one of its isomerides; it is a very stable compound, and is generally resinified by the reagents which have any action on it. The constitution of the above compounds is discussed at some length; the authors consider that lapachic acid, lapachone, and isolapachone are probably derivatives of α-naphthaquinone, and have respectively the structure represented by the formulæ I, II, III.



I.



II.



III.

Determinations of the molecular weights of nearly all the substances described were made by Raoult's method. S. B. A. A.

β-Dinaphthylcarbamide Chloride and β-Tetranaphthylcarbamide. By B. KÜHN and N. LANDAU (*Ber.*, **23**, 2161—2162).—A reply to Kym (this vol., p. 993), in which the authors give details of their experiments on the interaction of carbonyl chloride and β-dinaphthylamine in benzene-toluene solution at the ordinary temperature (compare Kym, this vol., p. 633, and Kühn and Landau, this vol., p. 634).

β-Tetranaphthylcarbamide melts at 287—288°, not at 167—169°, as previously stated. F. S. K.

Dinaphthyl Sulphides and Dinaphthylsulphones. By F. KRAFFT (*Ber.*, **23**, 2364—2369; compare Abstr., 1889, 715).—$\beta\beta$-Dinaphthylsulphone, $(C_{10}H_7)_2SO_2$, is prepared by oxidising $\beta\beta$-dinaphthyl sulphide (m. p. 151°) with a mixture of glacial acetic acid and potassium dichromate dissolved in dilute sulphuric acid; it is identical with the compound obtained by Stenhouse and Groves from naphthalene and sulphuric acid (compare this journal, 1876 ii, 517). It may be distilled under reduced pressure without undergoing decomposition. *$\alpha\alpha$-Dinaphthyl sulphoxide*, $(C_{10}H_7)_2SO$, is formed by gently warming $\alpha\alpha$-dinaphthyl sulphide (3 parts), dissolved in glacial acetic acid (250 parts), with a solution of potassium dichromate (3 parts) in dilute (1 : 3) sulphuric acid (20 parts) and glacial acetic acid (100 parts); it is deposited from alcohol in white crystals, melting at 164·5°, and is probably identical with the sulphoxide

(m. p. 162°) obtained by Ekstrand from naphthylene dinaphthyl sulphoxide (compare Abstr., 1885, 170), and also with the "sulphone" (m. p. 166°) prepared by Leükart from $\alpha\alpha$-dinaphthyl sulphide (compare Abstr., this vol., p. 603). *$\alpha\alpha$-Dinaphthylsulphone*, $(C_{10}H_7)_2SO_2$, is formed by oxidation of the corresponding sulphide (1 part) dissolved in glacial acetic acid (100 parts), with potassium dichromate (3 parts), dilute (1 : 3) sulphuric acid (15 parts), and glacial acetic acid (20 parts); it crystallises from alcohol, and melts at 187°. *$\alpha\beta$-Dinaphthyl sulphide*, $(C_{10}H_7)_2S$, is obtained by heating an intimate mixture of equivalent parts of α-bromonaphthalene and the lead salt of β-naphthyl hydrogen sulphide at 200—240° for about six hours; the product is treated with carbon bisulphide after purification; it crystallises from dilute alcohol in lustrous plates which melt at 60—61°, and boil at 290—291° under pressure of 15 mm. $\alpha\beta$-Dinaphthylsulphone, $(C_{10}H_7)_2SO_2$, is prepared by the oxidation of the sulphide; it melts at 122·5—123°, and is identical with the "α-sulphone" obtained by Stenhouse and Groves (*loc. cit.*). J. B. T.

Chrysene. By E. BAMBERGER and C. BURGDORF (*Ber.*, **23**, 2433—2446; compare Abstr., 1885, 1069).—The close analogy which has been shown to exist between the derivatives of phenanthraquinone and chrysoquinone has led the authors to endeavour to prepare the two unknown acids in the chrysene series, corresponding with diphenic acid and phenylbenzoic acid respectively. The diphenic acid analogue could not be obtained, as the oxidising agents employed invariably attacked the naphthalene nucleus as well as the carbonyl-group. Chrysoquinone is prepared by boiling chrysene (50 grams) with glacial acetic acid (1 kilo.) and gradually adding chromic anhydride (100 grams) dissolved in glacial acetic acid (1 kilo.); the operation should last 8—10 hours; the yield is 96—97 per cent. of the theory. Potassium permanganate acts more readily on chrysene, phthalic acid being the sole product. On distilling chrysoquinone over soda-lime, a complicated mixture was obtained, from which no definite compound, except chrysene, could be isolated. This result is opposed to the observations of Graebe, and of E. Schmidt, who prepared phenylnaphthalene (m. p. 104—105°) in this manner. The preparation of chrysoketone, $\begin{matrix} C_6H_4 \\ | \\ C_{10}H_6 \end{matrix}\!\!>\!CO$, has already been described (*loc. cit.*); it melts at 132·5°, not at 130° as stated, and crystallises from alcohol, on the addition of water, in thin, lustrous, golden needles; by fusion and subsequent cooling, thick, orange-red prisms are obtained; both forms belong to the rhombic system, the difference in appearance is due to pleichroism.

On heating chrysoquinone with 10 parts of potassium hydroxide at 225—230° for an hour, an acid is formed, crystallising from benzene in silvery-white, lustrous plates which melt at 186·5°; it readily dissolves in all the ordinary solvents except water, and is not acted on by dilute sulphuric acid at 200°. It yields chrysoketone by treatment with concentrated sulphuric acid. This compound, which the authors call *chrysenic acid*, is either naphthylbenzoic

acid, $C_{10}H_7 \cdot C_6H_4 \cdot COOH$, or phenylnaphthoic acid, $C_{10}H_6Ph \cdot COOH$; it is also obtained by the fusion of chrysoketone with potassium hydroxide. All attempts to prepare the corresponding hydrocarbon were unsuccessful. The barium salt, $C_{34}H_{22}O_4Ba + H_2O$, crystallises in stellate clusters of silvery, lustrous needles.

A second acid, *isochrysenic acid*, is formed by boiling chrysoketone with alcoholic potash for 8—10 hours. it is very soluble and extremely difficult to purify; on distillation with calcium hydroxide, it yields a hydrocarbon which crystallises from alcohol in lustrous, silvery-white plates melting at 181·5°.

Nitrochrysene may be readily prepared by warming a mixture of finely-divided chrysene (10 grams) with 10 parts of glacial acetic acid, and nitric acid (4·5 grams) of sp. gr. 1·415, for several hours on the water-bath. *Amidochrysene*, $C_{18}H_{11} \cdot NH_2$, is obtained by the action of tin and hydrochloric acid on a boiling glacial acetic acid solution of nitrochrysene; it is precipitated by alkalis from its salts as a white, crystalline powder melting at 199°. It quickly becomes coloured on exposure to air, and its solutions exhibit an intense blue-violet fluorescence. A dark-red dye is formed by the action of diazobenzenesulphonic acid on amidochrysene. The *platinochloride* is a yellow, crystalline substance. The *sulphate* and *hydrochloride* are very sparingly soluble.

J. B. T.

Camphene Glycol and Tetrahydric Alcohol from Limonene. By G. Wagner (*Ber.*, 23, 2307—2318).—It is first stated that a substance containing an ethylene linking loses this when oxidised with alkaline permanganate and adds on two hydroxyls, and this principle is then used to determine the existence of ethylene bonds in certain terpenes.

Camphene contains one ethylene linking, for it takes up two hydroxyl-groups and forms a glycol. A solution of camphene in the smallest possible quantity of benzene was poured into a large quantity of 1 per cent. permanganate solution and shaken until the pink colour disappeared. The mixture was then allowed to remain, and the clear alkaline liquid finally drawn off from the brown precipitate in a current of carbonic anhydride, and the residue washed with water. This was twice repeated. The alkaline solutions were saturated with carbonic anhydride and repeatedly extracted with benzene. The benzene was evaporated, the residue saturated with potash and extracted with ether, the ether extract evaporated, and the residue recrystallised from benzene. It was *camphene glycol*, $C_{10}H_{16}(OH)_2$, and formed prismatic needles of the monoclinic system, which sublime above 100° and melt, seemingly with slight decomposition, at 192°. It dissolves easily in ether, alcohol, carbon bisulphide, and chloroform, less easily in benzene. With acetic anhydride, it yields only a small quantity of a diacetyl-derivative, secondary reactions apparently taking place. It readily loses water, especially when heated with dilute hydrochloric acid; a solid substance, apparently isomeric with camphor, $C_{10}H_{16}O$, distils over with water, and when allowed to remain liquefies and becomes acid. It smells like camphor, but has marked aldehydic properties, reducing silver nitrate, &c. Its constitution is at present undetermined.

Limonene contains two ethylene linkings, for it takes up four hydroxyl-groups. A 1 per cent. permanganate solution was run slowly into a mixture of carvene and water, the mixture being continually shaken, and finally allowed to remain. The solution was filtered, the filtrate extracted with benzene, and distilled with water after the addition of some magnesium sulphate to prevent decomposition. The residue was concentrated and extracted with ether. A substance was thus obtained which, after recrystallisation from benzene, formed fine, brilliant, interwoven needles melting at 191·5—192°. It is *limonetrol*, a tetrahydric glycol, $C_{10}H_{16}(OH)_4$. It dissolves easily in water, and has a faintly sweet taste.

The paper contains some general remarks on the oxidation of saturated and unsaturated compounds, and attention is called to the fact that benzene-derivatives, when oxidised, behave like saturated, and not like unsaturated, fatty derivatives. C. F. B.

Terpenes and Ethereal Oils. By O. WALLACH (*Annalen*, **258**, 319—339; compare this vol., p. 169).—Further experiments have shown that cineolic acid (Abstr., 1888, 1205) has the composition $C_{10}H_{16}O_5$ previously assigned to it. The *methyl* salt, $C_8H_{14}O(COOMe)_2$, melts at 31°. The *anhydride*, $C_{10}H_{14}O_4$, is obtained when the acid is warmed with acetic anhydride; this crystallises from a mixture of benzene and light petroleum in long needles, melts at 77—78°, and boils at 157° under a pressure of 12—13 mm.; it is very soluble in chloroform and benzene, and is reconverted into the acid by boiling water.

When cineolic acid is subjected to dry distillation, it is decomposed into carbonic anhydride, water, a monocarboxylic acid of the composition $C_9H_{16}O_3$, and a neutral liquid; cineolic anhydride under the same conditions is decomposed quantitatively into carbonic oxide, carbonic anhydride, and the same neutral compound as that obtained from the acid. The neutral compound is separated from small quantities of anhydride by distillation with steam; it boils at 173—174° and has the molecular formula $C_8H_{14}O$, as was proved by analysis and by a vapour density determination. It has a penetrating odour very like that of amyl acetate, its sp. gr. is 0·8530 at 20°, and its refractive power is $n_D = 1·44003$. It combines readily with bromine and with halogen acids, and is decomposed by potassium permanganate in the cold, yielding carbonic anhydride and an unstable acid, but it does not decolorise a sulphurous acid solution of magenta; it combines with phenylhydrazine yielding an oil, and it forms a crystalline compound with sodium hydrogen sulphite. Its molecular refraction is 38·93, calculated for the formula $C_8H_{14}O$, from the data given above; employing Conrady's values, the molecular refraction of $C_8H_{14}O''|^{=} = 38·72$, whereas that of $C_8H_{14}O'|^{=} = 37·9$ and of $C_8H_{14}O'|^{\equiv} = 39·65$.

Metahydroxylene, C_8H_{12}, is obtained, together with a liquid boiling at 280—285°, which seems to be a polymeride thereof, when the compound of the composition $C_8H_{14}O$ is heated with zinc chloride at 90—95°; it is a liquid of sp. gr. 0·8275 at 20°, boils at 132—134°, and has an odour of xylene; its refractive power is $n_D = 1·4675$. It resembles the terpenes in many respects, and like them combines

readily with halogens and halogen acids; on oxidation with dilute nitric acid and potassium permanganate consecutively, it yields an acid which seems to be isophthalic acid. When carefully treated with ice-cold concentrated nitric acid, it yields nitrometaxylene, which was identified by converting it into metaxylidine; *diacetylmetaxylidine*, $C_6H_3Me_2\cdot NAc_2$, separates from light petroleum in well-defined crystals, melts at 60°, and is readily soluble in benzene. Metahydroxylene can also be converted into dinitrometaxylene (m. p. 90—91°) and trinitrometaxylene (m. p. 180—182°) by treating it with a mixture of concentrated sulphuric acid and nitric acid, first in the cold and then at 100°; the dinitro-compound was identified by reducing it to nitroxylidine (m. p. 123°) and converting the latter into its acetyl-derivative (m. p. 115—116°).

The formation of metaxylene from cineole in the manner described above might be considered as evidence in favour of the view that cineole, and the terpenes generally, contain two side-chains in the meta-position, especially as metaxylene has been previously obtained from pinene by Tilden (Trans., 1884, 416). The following arguments show, however, that this is not the case, and that the above series of reactions can be best explained by assuming that cineole has the constitution $CMe{<}\begin{matrix}CH_2\cdot CH_2\\ O\\ CH_2\cdot CH_2\end{matrix}{>}CPr^{\beta}$ assigned to it by Richter and accepted by Brühl. For, granting that cineole has this constitution and that its oxidation to cineolic acid is a reaction analogous to that which is generally assumed to take place in the formation of camphoric acid from camphor, the constitution of cineolic acid may be represented by the formula $\begin{matrix}CH_2\cdot CPr^{\beta}(COOH)\\ |\\ CH_2\cdot CMe(COOH)\end{matrix}{>}O$; this view would explain the formation of an anhydride and the conversion of cineolic acid into a monocarboxylic acid with evolution of carbonic anhydride. An anhydride of the constitution $\left|\begin{matrix}CH_2\cdot CPr^{\beta}\cdot CO\\ O\\ CH_2\cdot CMe\cdot CO\end{matrix}\right.{>}O$ might be decomposed into carbonic oxide, carbonic anhydride, and an unstable compound of the constitution $\begin{matrix}CH_2\cdot CPr^{\beta}\\ |\quad\ \ |\\ CH_2\cdot CMe\end{matrix}{>}O$, which might then undergo an intramolecular change, analogous to that which is supposed to take place in the formation of a pinacoline, and be converted into a ketone of the constitution $CHPr^{\beta}:CH\cdot CH_2\cdot COMe$. A ketone of this nature would probably have the properties possessed by the compound $C_8H_{14}O$, and it might be easily converted into metahydroxylene by the elimination of 1 mol. H_2O. The synthesis of the compound $C_8H_{14}O$ from a ketone of the above constitution will be attempted.

F. S. K.

Pinene. By O. WALLACH (*Annalen*, **258**, 343—347).—It has been previously shown (Abstr., 1889, 1069) that pinene nitrosochloride is decomposed by aniline in accordance with the equation

$C_{10}H_{16}{\cdot}NOCl + 2C_6H_5{\cdot}NH_2 = H_2O + HCl + N_2Ph{\cdot}C_6H_4{\cdot}NH_2 + C_{10}H_{16}$. The hydrocarbon obtained in this way has now been found to be chemically pure, inactive pinene; it boils at 155—156°, its sp. gr. is 0·858 at 20°, and its refractive power $n_D = 1{\cdot}46553$ at 21°. It remains inactive even when treated with hydrogen chloride, a fact which is more noteworthy since the inactive pinene obtained in other ways becomes lævorotatory under these conditions (compare Abstr., 1889, 1071) and probably consists, therefore, of equal parts of dextro- and lævo-pinene. Inactive pinene combines readily with nitrosyl chloride yielding the same products as the active modifications, namely, a crystalline nitrosochloride and pinole (compare Wallach and Otto, this vol., p. 169).

A liquid base of the composition $C_{10}H_{15}{\cdot}NH_2$ is obtained when nitrosopinene is treated with zinc and glacial acetic acid or with a mixture of hydriodic acid and glacial acetic acid; it boils at 207—208° (at 98—99° under a pressure of 22 to 23 mm.) and has an odour recalling that of borneol. The hydrochloride melts at 221—222°, and the benzoyl-derivative at 116°; the sulphate crystallises well. The investigation of this base is being continued.

F. S. K.

So-called Massoyene. By O. WALLACH (*Annalen*, **258**, 340—343).—The author has examined a sample of massoy-bark oil obtained from the same source as the oil investigated by Woy (this vol., p. 638); he finds that Woy's "massoyene" is not a new terpene but a mixture of various compounds, from which he isolated pinene. F. S. K.

Constituents of the Bark of Nerium oleander. By E. PIESZCZEK (*Arch. Pharm.*, **228**, 352—361).—By treating the bark with light petroleum, a liquid fat and a wax-like crystalline compound were extracted, which will be described later. The bark was then extracted with alcohol, the solution distilled to remove most of the alcohol, and filtered to remove a remnant of fat and a caoutchouc-like deposit. After several days, nodular aggregates of almost colourless, microscopic crystals formed. On recrystallisation from dilute alcohol, the substance was obtained as an almost colourless, soft, crystalline mass, insoluble in water, light petroleum, ether, and chloroform, easily soluble in alcohol. On warming with dilute hydrochloric acid, it gives the glucose reaction with copper solution, so that it is a glucoside. The alcoholic solution is not precipitated by tannin, platinic chloride, mercuric chloride, iodised potassium iodide, Nessler's reagent, lead acetate, or ammonia. It melts at 171°, then decomposes with separation of carbon, and burns with a smoky flame. It dissolves in concentrated sulphuric acid to a reddish-brown solution, not essentially changed by bromine vapour. *Rosaginin* is proposed as the name of the compound. It is exceedingly poisonous, resembling strychnine in its action. The mother liquor from the rosaginin contained *neriin*, a glucoside identical with the compound obtained by Schmiedeberg from the leaves of the same plant.

Small quantities of a volatile oil of disagreeable odour and a crystalline, fluorescent compound were also obtained. J. T.

Myrrh. By O. Köhler (*Arch. Pharm.*, **228**, 291—313).—The raw material consists of gum, resin, and an ethereal oil. The portion soluble in water, but insoluble in alcohol, amounting to 57 to 59 per cent. of the whole, is a gum of the carbohydrate formula, $C_6H_{10}O_5$, as shown by analysis and the formation of levulinic acid when heated with hydrochloric acid. The part soluble in alcohol is a mixture of several resins, the greater portion of which is a soft resin, $C_{26}H_{34}O_5$, containing three displaceable hydroxyl-groups, and is soluble in ether. There are also present two bibasic acids, $C_{13}H_{16}O_8$ and $C_{26}H_{32}O_9$ respectively. The ethereal oil, 7 to 8 per cent. of the whole, was found to consist mainly of the compound $C_{10}H_{14}O$. By doubling the formula of one of the acids, the three resinous constituents are seen to have each 26 atoms of carbon in their molecule, and the chief difference between them is probably due to oxidation. J. T.

Damascenine from Nigella damascena, L. By A Schneider (*J. Pharm.* [5], **22**, 58—61; from *Pharm. Centralhalle*, **21**, 173).—The crushed seeds of this plant are extracted with benzene, this is agitated with dilute hydrochloric acid, and the alkaloïd is precipitated by excess of sodium hydroxide and filtered off. A further crop is obtained by treating the filtrate with chloroform, extracting this with dilute hydrochloric acid, and precipitating with sodium hydroxide. The product is purified by dissolving it in absolute alcohol and evaporating over sulphuric acid in a vacuum, when a thick, brownish-yellow, fluorescent liquid is left which gives large crystals of an alkaloïd, *damascenine*, when placed in a freezing mixture. These crystals are dried between blotting-paper in the cold, as the heat of the hand melts them. The yield is about 0·1 per cent. *Nigella sativa* and *N. arvensis* do not appear to contain the alkaloïd. The crystals are slightly yellow, with a bluish fluorescence and a narcotic odour; their reaction is alkaline; they melt at 27° and recrystallise on cooling. The fused compound forms a yellowish, feebly fluorescent oil of sp. gr. 1·01, and gives a greasy stain on paper which disappears on heating. It boils at 168°, but emits vapours at the ordinary temperature. The alkaloïd is insoluble in cold water, slightly soluble in hot water, easily soluble in alcohol, chloroform, methyl alcohol, carbon bisulphide, benzene, light petroleum, and in the fatty oils. All these solutions have a blue fluorescence, which, in the case of benzene, is perceptible with 1 : 200,000. Damascenine dissolves readily in dilute acids. These solutions, which are not fluorescent, yield amorphous precipitates with the ordinary reagents of the alkaloïds. A characteristic reaction is the beautiful reddish-violet colour produced by long contact of the alkaloïd with excess of concentrated nitric acid. *Damascenine hydrochloride* is obtained by adding concentrated hydrochloric acid to a solution of the alkaloïd in absolute alcohol, and then adding ether until the precipitate formed just ceases to dissolve on shaking. On standing, the salt crystallises out. The crystals melt at 121°. The nitrate and sulphate are prepared in a similar manner. Analysis of the alkaloïd points to the formula $C_{20}H_{15}NO_6$. J. T.

Ferrocyanides of the Alkaloïds. By H. BECKURTS (*Arch. Pharm.*, **228**, 347—352).—According as the decomposition of the alkaloïd salts by potassium ferrocyanide takes place in neutral or acid aqueous solutions, the resulting alkaloïd ferrocyanide is normal or acid. The acid ferrocyanides are prepared by dissolving the alkaloïd in concentrated hydrochloric acid, and adding the least possible excess of a concentrated aqueous solution of potassium ferrocyanide; the resulting precipitate is washed and dried. The following acid ferrocyanides were produced. *Atropine* salt, $C_{17}H_{23}NO_3,H_4FeC_6N_6$; amorphous powder, soluble in water and potassium ferrocyanide solution, insoluble in alcohol and ether. *Quinine* salt, $C_{20}H_{24}N_2O_2,H_4FeC_6N_6$; greenish, amorphous powder, soluble in much water and in potassium ferrocyanide solution, insoluble in alcohol, ether, and chloroform. *Quinidine* salt; yellowish-white, crystalline powder, sparingly soluble in water, insoluble in chloroform, alcohol, and ether. *Cinchonine* salt; orange-yellow, crystalline powder, sparingly soluble in water, insoluble in alcohol, ether, and chloroform. *Cinchonidine* salt; reddish-yellow, crystalline powder, sparingly soluble in water. *Cocaïne* salt,

$$(C_{17}H_{21}NO_4)_2,H_4FeC_6N_6;$$

white, amorphous powder, easily soluble in excess of potassïum ferrocyanide solution, sparingly soluble in water, insoluble in alcohol and ether. *Coniine* salt; amorphous, white powder. *Hydrastine* salt; white, amorphous, sparingly soluble powder. *Morphine* salt; white, crystalline powder, easily soluble in water; becomes pale-blue in the air. *Narceïne* salt; bluish-white, crystalline powder, somewhat sparingly soluble in water. *Narcotine* salt; bluish-white, crystalline, voluminous powder, easily soluble in water. *Pilocarpine* salt; white, crystalline powder, easily soluble in water. *Sparteïne* salt; white, crystalline powder, easily soluble in water. *Strychnine* salt; white, crystalline powder with a bluish shade, insoluble in cold water and alcohol, decomposed by hot water with separation of hydrogen ferrocyanide. *Brucine* salt; white, microscopic, prismatic crystals which quickly turn blue in the air; dilute solutions gradually deposit large, white prisms. J. T.

Reduction-products of Quinoline. By E. BAMBERGER and F. LENGFELD (*Ber.*, **23**, 1138—1158).—When tetrahydroquinoline hydrochloride (3 grams) is heated with hydriodic acid (sp. gr. = 1·9) (16 grams) and red phosphorus (1·75 grams) at 230° for 3—4 hours, a product is obtained consisting of 55 per cent. of decahydroquinoline and 8 per cent. of hexahydroquinoline, together with about 0·25 per cent. of a hydrocarbon, possibly propylhexamethylene, and a third base which has not yet been examined and is not volatile with steam. To separate it into its constituents, the product is rendered alkaline and submitted to steam distillation until the distillate comes over neutral and gives no colour with potassium dichromate or ferric chloride in acid solution. The distillate is acidified with hydrochloric acid, extracted with ether to remove the insoluble hydrocarbon, evaporated to a small bulk, rendered alkaline, and the separated bases dissolved in ether. The ethereal solution, on evaporation, leaves an

oil from which the decahydro-base is separated by extraction with very weak acetic acid, the hexahydro-base remaining undissolved.

Decahydroquinoline, C_9NH_{17}, is best purified by distillation under the ordinary pressure. It crystallises from water or light petroleum in thin, colourless prisms, melts at 48·2—48·5°, boils at 204° (therm. in vapour) under 714 mm. pressure, has a very intense basic odour extremely like that of coniine, and readily absorbs carbonic anhydride from the air. It is very volatile even with ether vapour, sublimes at the ordinary temperature in lustrous aggregates of needles, is not only very soluble in the ordinary organic solvents, but also in water, dissolves sparingly in alkalis, gives no colour reactions with potassium dichromate, ferric chloride, or diazo-compounds, and in physiological action resembles piperidine. Its aqueous solution has a strong alkaline reaction. The salts, which are anhydrous, crystallise well, and for the most part are readily soluble in water forming neutral solutions. The *hydrochloride*, C_9NH_{17},HCl, crystallises in small, colourless, lustrous, rhombic tables, melts at 275·5—276°, and is very soluble in alcohol and water; the *aurochloride*, $C_9NH_{17},HAuCl_4$, forms small, golden-yellow needles, melts at 96°, and is soluble in alcohol and chloroform, sparingly soluble in cold water, and insoluble in benzene and light petroleum; the *platinochloride*, $(C_9NH_{17})_2,H_2PtCl_6$, crystallises in lustrous, orange-red, thick prisms, melts at 207—207·5° with decomposition, and is readily soluble in water, insoluble in alcohol, chloroform, benzene, &c.; the *hydriodide*, C_9NH_{17},HI, forms long, silky needles, melts at 253°, and is somewhat less soluble in water than the hydrochloride; the *hydrogen sulphate* crystallises in very soluble, flat needles, and the *picrate* in yellow needles. The *acetyl*-derivative, $C_9NH_{16}Ac$, is a colourless, viscid oil, dissolves readily in the ordinary solvents, including water, and does not combine with bromine; the *benzoyl*-derivative, $C_9NH_{16}Bz$, crystallises in lustrous, white needles, melts at 44°, and is readily soluble in the ordinary organic solvents, sparingly soluble in water. The *nitrosamine*, $C_9NH_{16}{\cdot}NO$, is a yellow, viscid liquid which dissolves readily in concentrated acids and the ordinary organic solvents, sparingly in water, gives a grass-green colour when mixed with phenol and sulphuric acid and subsequently treated with alkali, and regenerates the base when hydrogen chloride is passed into its ethereal solution. The *diazoamido*-compound, $C_9NH_{16}{\cdot}N_2{\cdot}Ph$, crystallises from ether in flat, lustrous tables resembling crystals of alloxan, from alcohol in stellate groups of silver-white needles, melts at 78·6°, dissolves readily in the ordinary organic solvents, and yields phenol and decahydroquinoline with the evolution of nitrogen when warmed with mineral acids. The *phenylthiocarbamide*, $C_9NH_{16}{\cdot}CS{\cdot}NHPh$, crystallises from chloroform in beautiful, rhombic tables, melts at 134·5°, and is readily soluble in chloroform, alcohol, and benzene, sparingly soluble in ether, and almost insoluble in water and light petroleum; the *phenylcarbamide*, $C_9NH_{16}{\cdot}CO{\cdot}NHPh$, crystallises from alcohol in lustrous, silvery needles, melts at 148°, and in solubility resembles the thio-compound. The *decahydroquinolyldithiocarbamate*, $C_9NH_{16}{\cdot}CS{\cdot}SH,C_9NH_{17}$, forms lustrous, white, flat needles, melts at 120°, dissolves readily in alcohol, chloroform, benzene, and hot water, sparingly in ether and cold

water, is not decomposed by prolonged boiling with alcohol, and yields the *thiuramsulphide*, $C_9NH_{16}·CS·S_2·SC·C_9NH_{16}$, on treatment in alcoholic solution with iodine.

Hexahydroquinoline, C_9NH_{13}, is a colourless, viscid liquid, boiling at 226° under 720 mm. pressure. It has a neutral reaction, resembles quinoline in odour, is readily soluble in the ordinary organic solvents, sparingly soluble in water, gives brown flocks when treated with potassium dichromate or ferric chloride in acid solution, and is converted into a bright-red azo-dye by the action of diazobenzenesulphonic acid. In physiological action it resembles quinoline more closely than decahydroquinoline. The *hydrochloride*, C_9NH_{13},HCl, forms white, silky needles, melts at 170°, and is readily soluble in alcohol and water, sparingly soluble in hydrochloric acid; the *hydrobromide* crystallises in long, silky needles.

The hydrocarbon formed in the reduction of tetrahydroquinoline, and provisionally regarded as *propylhexamethylene*, is a colourless, mobile liquid of pleasant aromatic odour, boiling at 146—148° (therm. in vapour) under 720 mm. pressure. W. P. W.

Bromo-derivatives of Quinoline. By A. CLAUS and A. WELTER (*J. pr. Chem.* [2], **42**, 233—247; see also this vol., p. 173).—1 : 4'-*Dibromoquinoline*.—To prepare this compound, 1-bromoquinoline is converted by Claus and Tornier's method (Abstr., 1888, 163) into the additive compound, C_9NH_6Br,HBr,Br_2, a red, crystalline mass which melts at 70° with decomposition. On heating this compound in a retort at 200° for 4—6 hours, a mixture of hydrobromides and free bromoquinolines sublimes, which is treated with soda and distilled in a current of steam, and the 1 : 4'-dibromoquinoline separated from the solution of the distillate in hydrochloric acid by fractional precipitation with water. On recrystallisation from alcohol, it forms silky needles which melt at 101—102° (uncorr.), and are readily soluble in ether, alcohol, and chloroform.

1 : 4'-Dibromoquinoline may also be obtained from 1-nitroquinoline by acting on it with bromine in hydrobromic acid solution, and heating the additive product in a retort at 200°. Its *hydrochloride*, $C_9NH_5Br_2,HCl$, forms large, well-developed prisms which melt at 141—142°, are not stable in the air, and are decomposed by alcohol and water. The *sulphate* melts at 206°, the *chromate* at 158° with decomposition, whilst the *platinochloride* remains unaltered at 280°, but blackens at a higher temperature.

Nitro-1 : 4'-*dibromoquinoline*, $C_9NH_4Br_2·NO_2$, is obtained by the action of a mixture of sulphuric and nitric acids on the foregoing compound. It is very sparingly soluble in alcohol, readily in ether, chloroform, and concentrated mineral acids, crystallising out unaltered from the latter. Its *platinochloride* forms short, six-sided prisms. On reduction, it yields *amido*-1 : 4'-*dibromoquinoline*, $C_9NH_4Br_2·NH_2$, which crystallises in small, colourless needles melting about 170°, readily soluble in alcohol, ether, chloroform, and even in hot water. It assumes an intense red coloration when acted on by hydrogen chloride. The *hydrochloride* crystallises in long, red needles melting at 214—215°, and the *platinochloride* in beautiful, yellow needles.

1 : 4 : 4′-*Tribromoquinoline*, $C_9NH_4Br_3$.—This compound, which was formerly described as γ-tribromoquinoline, is the most frequent product of the further bromination of quinoline. Its constitution has been ascertained by its synthetical formation, the manner of which will be described in a later paper. It is best prepared by heating 4′-bromoquinoline with bromine and water at 130—150°, substitution-products being thus almost exclusively formed. To isolate the 1 : 4 : 4′-tribromoquinoline, the product is distilled in a current of steam, and the different distillates fractionally precipitated from their hydrochloric acid solution by water; the higher brominated products first separating, and then the tribromo-compound. On recrystallisation from alcohol, it melts constantly at 167° (uncorr.), and is readily soluble in ether and chloroform, and in concentrated acids. If it be dissolved in concentrated nitric acid, reprecipitated by water, and again recrystallised from alcohol, it forms long, silky needles melting at 169—170°. It volatilises with difficulty in a current of steam, sublimes without decomposition, and is not acted on by methyl iodide at 140°. Its *hydrochloride* forms silvery scales which are decomposed by water, alcohol, and dilute acids. The *platinochloride* has also been prepared. On oxidation, the base is completely converted into bromine, carbonic anhydride, nitrogen, and water; it is unaltered by dilute boiling aqueous potash. Alcoholic potash and concentrated aqueous potash at 230—250° attack it, the bromine being apparently displaced by hydroxyl.

By the action of a mixture of sulphuric and fuming nitric acids, preferably at 100°, it yields a mixture of two nitro-derivatives, which may be separated by taking advantage of the difference in their solubility in alcohol. The first compound remains as a green, pulverulent mass when the product of the reaction is extracted with alcohol, and it is also insoluble in ether, dilute and concentrated mineral acids, but it crystallises from chloroform in beautiful, six-sided tablets, or prisms, which melt at 215—216°. On reduction with alcoholic hydrochloric acid and stannous chloride, it yields the stannochloride of the corresponding amido-compound, $C_9NH_3Br_3{\cdot}NH_2,HSnCl_3$, crystallising in red prisms or needles, which on successive treatment with hydrogen sulphide and soda, yield the free base. The latter may be extracted with ether, and the residue remaining on evaporation washed with a little water, and crystallised from alcohol. Thus obtained, it forms yellow, plastic needles melting at 196°, scarcely soluble in hot water, readily in alcohol, ether, and chloroform. Its *hydrochloride* is very unstable, and forms blood-red prisms, and the *platinochloride* forms yellow or red, four-sided tablets or prisms which are decomposed by water.

The second nitro-1 : 4 : 4′-tribromoquinoline is obtained from the alcoholic extract, and crystallises in small, white, silky needles which quickly become yellow or green. It melts at 195°.

The residue in the retort, after distilling the product of the reaction of bromine on 1-bromoquinoline in a current of steam, yields on solution in hydrochloric acid, and fractional precipitation with water, a *tetrabromoquinoline*, $C_9NH_3Br_4$, which crystallises in slender, white needles melting at 197—198°. It does not appear to form salts.

In the more volatile portions of the steam distillate 4 : 4′-dibromoquinoline was also identified. H. G. C.

Conversion of the Homologues of Indole into Quinoline-derivatives. By G. MAGNANINI (*Gazzetta*, 19, 569—577).—*Methylquinoline.*—When methylketole is heated in a sealed tube with concentrated hydrochloric acid for 6 to 7 hours at 220—230°, and the product is freed from hydrochloric acid, steam distilled, made alkaline, and redistilled, a mixture of aniline with another basic compound passes over. The new base, when pure, boils at 250°, and has a strong odour of quinoline. It is a tertiary base, and does not yield a nitroso-derivative with potassium nitrite and sulphuric acid. The *platinochloride*, $(C_{10}NH_9)_2,H_2PtCl_6$, and the *aurochloride*, $C_{10}NH_9,HAuCl_4$, are well crystallised salts.

Chloroquinaldine, $C_{10}NH_8Cl$, is prepared by gradually adding chloroform to a mixture of methylketole and sodium ethoxide. The action is very violent, the product being partially resinified, but heat must be applied to complete the reaction. The pure base, obtained by decomposing the picrate, crystallises from dilute boiling alcohol in very slender, thin, white needles, melts at 71—72°, and smells strongly of quinoline. It shows feeble basic properties; the *platinochloride* crystallises in orange needles; the *picrate* is a sparingly soluble salt, which crystallises in yellow needles, and melts at about 223° with decomposition.

Bromoquinaldine is prepared in a manner analogous to the chlorinated derivative, and has very similar properties; it crystallises from alcohol in white needles, and melts at 78°; the *picrate* crystallises in monoclinic, colourless needles, $a : b : c = 0.90992 : 1 : 0.62391$, $\beta = 64° 31' 33''$; faces observed (110), (001), ($\bar{1}11$). It melts into a black liquid at 224—225°. When bromoquinaldine is heated with hydriodic acid and amorphous phosphorus for 5—6 hours at 180°, it loses bromine, and a base is left which smells strongly of quinaldine, and forms a *picrate* melting at 191° and a methiodide melting at 195°; the latter gives a carmine coloration with a concentrated solution of potash, exactly like the quinaldine methiodide obtained by Doebner and Miller (Abstr., 1884, 183). The base is probably quinaldine, but no analysis was made, on account of want of material.

Chlorolepidine, $C_{10}NH_8Cl$, isomeric with chloroquinaldine and with Knorr's chlorolepidine (Abstr., 1887, 159), is obtained by the action of chloroform on scatole; it crystallises from dilute boiling alcohol in silky needles melting at 54—55·2°; the *picrate* is a very sparingly soluble, yellow compound, melting at 208—208·5°; the *aurochloride* melts at 163·5—164·5°.

Bromolepidine, obtained by the action of bromoform on scatole, melts at 58·5—59·5°, and its properties are analogous to those of the previous bases; the *picrate* melts with decomposition at 214—215°. The author considers his chloroquinaldine and chlorolepidine to be 3′ : 2′- and 3′ : 4′-chloromethylquinolines respectively.

S. B. A. A.

The Halogen Alkyloxides of Orthohydroxyquinoline and Parahydroxyquinoline. By A. CLAUS and H. HOWITZ (*J. pr. Chem.* [2], 42, 222—232).—Lippmann and Fleissner, in their investigation of the action of methyl iodide on orthohydroxyquinoline, came to the conclusion that the reaction does not proceed in the normal manner, but that a molecular compound of methoxyquinoline hydriodide and hydroxyquinoline methiodide, $C_9NH_6(OMe),HI + C_9NH_6(OH),MeI$, is formed, as on treatment with alkali they found that only half of the iodine was readily removed, a compound being formed to which they gave the formula $C_{19}H_{20}N_2O_2I$. The authors have repeated these experiments, and find the additive compound is readily obtained by heating orthohydroxyquinoline and methyl iodide in a sealed tube at 100° without any solvent. It crystallises from water in lustrous, yellow tablets of the composition $C_9NH_6(OH)MeI + H_2O$, and has all the properties mentioned by Lippmann and Fleissner. The corresponding chloride was also prepared from the iodide by treatment with silver chloride, and its molecular weight ascertained by Raoult's method. This agreed with the simple formula given above, and not with the double formula of Lippmann and Fleissner. It would, therefore, appear that, on treatment with alkalis, 2 mols. of the methiodide must take part in the reaction in the following manner:—

$$HO{\cdot}C_9NH_6MeI + HO{\cdot}C_9NH_6MeI = HO{\cdot}C_9NH_6Me{\cdot}O{\cdot}C_9NH_6MeI.$$

In confirmation of this supposition the authors find that hydriodic acid reconverts this iodide into the original methiodide, and that with hydrochloric acid it yields a mixture of the methiodide and methyl chloride in molecular proportion, whereas, if Lippmann and Fleissner's supposition were correct, the hydrochloride of the compound $C_{19}H_{20}N_2O_2I$ should have been formed.

Lippmann and Fleissner also state that methyl iodide converts this iodide into a new compound of the formula $C_{21}H_{22}N_2O_2I_2 + 2H_2O$, whereas, according to the authors' views, this should consist of a mixture of hydroxyquinoline methiodide and methoxyquinoline methiodide. The fractional crystallisation of the product from water has shown that such is really the case, the above-mentioned compounds having both been isolated and compared with the compounds obtained directly by the usual reactions. Orthomethoxyquinoline methiodide, $MeO{\cdot}C_9NH_6MeI + H_2O$, crystallises in pale-yellow, lustrous prisms, which lose their water of crystallisation at 100°, become red at 120°, and melt, with complete decomposition, at 160°. It does not lose hydrogen iodide on treatment with potash in the cold.

Parahydroxyquinoline also combines with methyl iodide, forming a *methiodide*, $HO{\cdot}C_9NH_6MeI,H_2O$, which crystallises from water in reddish-yellow prisms. These lose their water of crystallisation at 100°, and commence to decompose at 225—230°. From alcohol it crystallises in greenish-yellow, anhydrous plates. The corresponding *parahydroxyquinoline methochloride*, $HO{\cdot}C_9NH_6MeCl$, is obtained by treating the iodide with silver chloride, and crystallises from water in large, yellowish prisms, which also contain 1 mol. H_2O. Unlike the ortho-compounds, these substances readily lose all the halogen

on treatment even with ammonia, the compounds formed being at present under examination. H. G. C.

Acid Derivatives of Orthamidoquinoline. By G. M. KYRITZ (*Arch. Pharm.*, **228**, 362—373).—Satisfactory results in the preparation of an orthonitroquinoline and its derived amido-quinolines can be obtained with commercial quinoline (coal-tar quinoline) when it is freed from its homologues by fractional distillation and conversion into the zinc double salt. The quinoline is then nitrated and freed from para- and meta-nitroquinoline by partial fractional precipitation and recrystallisation from alcohol. The nitroquinoline is reduced with stannous chloride and hydrochloric acid, the resulting base set free by the addition of sodium hydroxide, and distilled over with steam from a metallic retort, when a greater yield is obtained than if a glass retort is employed. The base is precipitated from the distillate with picric acid, and the picrate is decomposed by means of potassium hydroxide, taken up in ether, neutralised with sulphuric acid, freed from ether by evaporation, again set free by sodium hydroxide, and distilled off. Scaly, white plates of orthamidoquinoline, $C_9NH_6\cdot NH_2$ are thus obtained, which melt at 67°. *Acetorthamidoquinoline*, $C_9NH_6\cdot NHAc$, is produced by heating the amido-compound with acetic anhydride for 20 hours on the oil-bath. The brown mass poured into hot water, heated with animal charcoal, and filtered, gives long, white crystals which melt at 102·5°. Acetic chloride, and also glacial acetic acid, yields the same result. The compound has a bitter taste, is very soluble in 95 per cent. alcohol, also in ether, benzene, and chloroform. In cold water it is sparingly soluble; in hot water it is relatively easily soluble. At a temperature above 300°, it distils without decomposition.

Phthalylorthamidoquinoline, $C_9NH_6\cdot N\colon(CO)_2\colon C_6H_4$, is produced by the action of phthalic anhydride on the amido-base. At 85° to 88° the mixture suddenly froths up; it is then heated at 130° for $1\frac{1}{2}$ hours, the excess of phthalic anhydride is removed by means of benzene, the dried residue dissolved in hot alcohol, decolorised by animal charcoal, and set to crystallise. The phthalyl compound forms small, white crystals, which melt at 227·5°. It is almost insoluble in cold and hot water. Alcohol dissolves it on long boiling; hot chloroform and ether dissolve it somewhat easily; in cold ether it is almost insoluble. Warmed with sulphuric acid, it is decomposed into its constituents. Its boiling point is above 200°. J. T.

Regularities in the Oxidation of Quinoline-derivatives. By W. v. MILLER (*Ber.*, **23**, 2252—2273).—The behaviour of various alkyl-derivatives of quinoline, on oxidation with chromic acid in warm dilute sulphuric acid, has been examined, and is described below; from the results obtained by the author and many others the following general conclusions may be drawn:—

All methyl- and ethyl-quinoline-derivatives in which the alkyl radicle is situated in the pyridine nucleus are oxidised by chromic acid to the corresponding quinolinecarboxylic acid; longer side chains are also converted into the carboxyl-group.

When there are two methyl-groups in the pyridine-ring, the radicle in the 4′-position is most readily, that in the α-position less readily, oxidised; 3′ : 4′-dimethylquinoline, for example, is converted into 3′-methylcinchoninic acid.

A methyl-group in the pyridine ring is less readily oxidised than one situated in the benzene nucleus; this is also true, even when the side chain in the pyridine ring is the longer of the two, provided it is in the 2′-position.

Of two alkyl radicles, both of which are in the pyridine ring, the one of higher molecular weight is the more readily oxidised.

When two methyl-groups are present in the pyridine, and one in the benzene nucleus, the latter is oxidised first; 2′-ethyl-3′-methyl-3-toluquinoline forms an exception to this rule (see below).

A methyl-group in the ortho-position in the benzene nucleus is not so readily oxidised as the same radicle in the para-position.

It seems, therefore, that as regards methyl-groups, the order of stability is as follows:—α-, β-, γ-, ortho-, meta-, and para- (=2′, 3′, 4′, 1, 2, 3), the radicle in combination with the nitrogen-atom being the most readily oxidised. When a carboxyl-group is present in one nucleus, a saturated side chain in the other ring is only oxidised with difficulty.

3′-Methylcinchoninic acid, $C_{11}H_9NO_2$, is formed when 3′ : 4′-dimethylquinoline is oxidised with chromic acid. It crystallises from water in colourless, microscopic plates, melts at 254°, and is readily soluble in hot water, but only moderately easily in alcohol, and insoluble in ether, benzene, and light petroleum; on distillation with soda-lime, it yields 3′-methylquinoline.

Orthotoluquinaldine hydrochloride crystallises in colourless needles, the *picrate*, $C_{11}H_{11}N,C_6H_3N_3O_7$, in golden plates, and the *nitrite*, $C_{11}H_{11}N,HNO_2$, in needles; when the base is oxidised with chromic acid, it is converted into quinaldineorthocarboxylic acid (m. p. 151°).

Benzylidenequinoline-3-carboxylic acid, $C_{18}H_{13}NO_2$, prepared by heating quinaldineparacarboxylic acid with benzaldehyde at 130—150°, in presence of zinc chloride, crystallises from hot dilute acetic acid in yellow needles, melts at 264°, and is insoluble in most ordinary solvents except hot dilute alcohol, acetic acid, and alkalis; on oxidation with chromic acid, it yields a yellow, crystalline acid, $C_{11}H_7NO_4$, which turns brown at 265°, and melts at 275—280° with decomposition.

Quinaldine-3 : 4′-dicarboxylic acid, $C_{12}H_9NO_4$, was obtained as a colourless powder by heating acetaldehyde with paramidobenzoic acid and pyruvic acid in alcoholic solution. It softened at about 260°, but had no definite melting point; when heated it yields quinaldine. The copper salt, $C_{12}H_7NO_4Cu$, is crystalline.

Ethylquinoline-3 : 4′-dicarboxylic acid, $C_{13}H_{11}NO_4$, prepared in like manner from propaldehyde, is a colourless, amorphous powder.

When metatoluquinaldine is oxidised with chromic acid, it is converted into quinaldine-2-carboxylic acid (m. p. 284°); paratoluquinaldine, under the same conditions, yields quinaldine-3-carboxylic acid (m. p. 256°), the *platinochloride* of which has the composition $(C_{11}H_9NO_2)_2,H_2PtCl_6 + 4H_2O$.

4′-Methyl-3-toluquinoline, formed by the condensation of para-

toluidine with acetone and paraformaldehyde, is an agreeably smelling oil, boiling at 273—274°; the *platinochloride*, $(C_{11}H_{11}N)_2,H_2PtCl_6 + 2H_2O$, crystallises from concentrated hydrochloric acid in needles, and melts at 238°. When the base is oxidised with chromic acid, it is converted into a methylquinolinecarboxylic acid, $C_{11}H_9NO_2$, and a very small quantity of another acid, which was not analysed. The former crystallises from hot water in needles, melts at 250—270° with decomposition, and yields lepidine on distillation with soda-lime.

3-*Methyl-2'-ethylcinchoninic acid*, $C_{13}H_{13}NO_2$, obtained by the condensation of paratoluidine with propaldehyde and pyruvic acid, crystallises from hot alcohol in microscopic plates, sinters together at 242°, and melts at 244—248° with decomposition; it is sparingly soluble in cold water and alcohol, but readily in hot alcohol. The *barium* salt, $(C_{13}H_{12}NO_2)_2Ba$, crystallises from water in yellow plates; the *silver* salt, $C_{13}H_{12}NO_2Ag$, is gelatinous. The *hydrochloride* crystallises in long needles. When the acid is distilled, it yields 2'-ethyl-3-toluquinoline, identical with the base obtained by Harz (Abstr., 1886, 261). The compound of the composition $C_{13}H_{13}NO$ (*loc. cit.*) is the aldehyde of 3-methyl-2'-ethylquinoline-3'-carboxylic acid.

When 2'-ethyl-3-toluquinoline is oxidised with chromic acid, it is converted into a resinous acid melting at about 235°, which, on distillation with soda-lime, yields 2'-ethylquinoline.

2'-*Ethyl-3'-methylquinoline*-1-*carboxylic acid*, $C_{13}H_{13}NO_2$, is formed by the oxidation of 2'-ethyl-1 : 3'-dimethylquinoline. It separates from hot alcohol in crystals, melts at 215—216°, and is only sparingly soluble in hot water, but more readily in hot alcohol. The *barium* salt, $(C_{13}H_{12}NO_2)_2Ba + \frac{1}{2}H_2O$, crystallises in plates, and is moderately easily soluble in water. When the acid is distilled over soda-lime, it yields 2'-ethyl-3'-methylquinoline (m. p. 55—56°).

3 : 2' : 3'-*Trimethylquinoline*, $C_{12}H_{13}N$, the condensation-product of tiglic aldehyde and paratoluidine, separates from light petroleum in large, nodular crystals, melts at 86—87°, and boils at 285°; it is readily soluble in ether, but only sparingly in benzene and light petroleum, and insoluble in water. The *platinochloride*,

$$(C_{12}H_{13}N)_2,H_2PtCl_6 + 2H_2O,$$

crystallises in brown plates, the *chromate* in orange-red plates, and the *picrate* in yellow plates, melting at 212° with decomposition. The *hydrochloride* and the *sulphate* are very readily soluble in water, but the *nitrate* is more sparingly soluble. On oxidation, the acid is converted into 2' : 3'-dimethylquinoline-3-carboxylic acid, $C_{12}H_{11}NO_2$; this compound crystallises in needles, sinters together at 258°, melts at 270° with decomposition, and yields 2' : 3'-dimethylquinoline (m. p. 67—68°) on distillation with soda-lime.

1 : 3 : 3'-*Trimethyl-2'-ethylquinoline*, $C_{14}H_{17}N$, can be obtained by the condensation of asymmetric metaxylidine with propaldehyde. It crystallises from hot alcohol in plates, melts at 62°, boils at 291°, and is volatile with steam; it is readily soluble in ether, benzene, and light petroleum, but more sparingly in alcohol. The *picrate*, $C_{14}H_{17}N,C_6H_3N_3O_7$, crystallises from hot alcohol in yellow

needles; the *platinochloride*, $(C_{14}H_{17}N)_2.H_2PtCl_6$. *nitrate, sulphate*, and *dichromate* are crystalline. The *hydrochloride*, $C_{14}H_{17}N,HCl + 3H_2O$, crystallises in colourless needles. The *methiodide*, $C_{14}H_{17}N,MeI$, crystallises in yellowish needles, and is soluble in hot water and alcohol. The *nitro*-derivative, $C_{14}H_{16}N\cdot NO_2$, crystallises from alcohol in needles, melts at 90°, and is readily soluble in ether, benzene, and light petroleum, but only sparingly in water. The *dinitro*-compound, $C_{14}H_{15}N(NO_2)_2$, crystallises from hot alcohol in colourless plates, and melts at 152·5°. The *sulphonic acid*, $C_{14}H_{16}N\cdot SO_3H$, crystallises in small, colourless needles, and is sparingly soluble in water.

Ethyltrimethyltetrahydroquinoline, $C_{14}H_{21}N$, prepared by reducing the base just described, is an oil boiling at 287—289°; it forms an *acetyl*- and a *nitroso*-derivative. The *picrate*, $C_{14}H_{21}N,C_6H_3N_3O_7$, melts at 146°.

3 : 3′-*Dimethyl*-2′-*ethylquinoline*-1-*carboxylic acid*, $C_{14}H_{15}NO_2$, is formed when the ethyltrimethyl base is oxidised with chromic acid; it separates from alcohol in colourless crystals, melts at 182—183°, and is readily soluble in alcohol and water, but sparingly in benzene and chloroform, and insoluble in ether; on distillation with soda-lime, it is converted into 3 : 3′-dimethyl-2′-ethylquinoline (compare Harz, *loc. cit.*).
F. S. K.

Action of Phenylhydrazine on Pyrocinchonic, α-Dichloro-symmetrical-dimethylsuccinic, and α-Dichloropropionic Anhydrides, and on Pyrocinchonic Chloride. By R. Otto and G. Holst (*J. pr. Chem.* [2], **42**. 65—81; compare Abstr., 1887, 669).—When solutions of pyrocinchonic anhydride (1 mol.) and phenylhydrazine (2 mols.) in a little benzene are mixed, *phenylhydrazine pyrocinchonylphenylhydrazinate*, $\begin{matrix}\text{MeC}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}\\ \parallel\\ \text{MeC}\cdot\text{COO}\cdot\text{NH}_3\cdot\text{NHPh}\end{matrix}$, is produced as a bulky precipitate, which dries to a white, crystalline powder, but cannot be recrystallised (see below); dilute hydrochloric acid decomposes it into phenylhydrazine hydrochloride and pyrocinchonic anhydride. When it is heated at 110—120°, it decomposes into water, phenylhydrazine, and a substance which melts at 129°; the latter, *β-pyrocinchonylphenylhydrazine*, is most easily obtained by dissolving the phenylhydrazinate in hot dilute alcohol; on cooling the solution, the new substance crystallises out.

β-Pyrocinchonylphenylhydrazine, $\begin{matrix}\text{MeC}\cdot\text{CO}\cdot\text{NH}\\ \parallel \qquad\quad |\\ \text{MeC}\cdot\text{CO}\cdot\text{NPh}\end{matrix}$, forms beautiful, yellow, monosymmetrical prisms (crystallography given), which melt at 129°, and are insoluble in water, but soluble in most other solvents. Its constitution is settled by the close analogy which its preparation bears to that of Hötte's β-phthalylphenylhydrazine (Abstr., 1887, 669). Hötte, however, did not obtain a *phenylhydrazine β-phthalylphenylhydrazinate*, so to complete the chain of evidence the author has prepared this substance; it separates from a hot alcoholic solution as a white, prismatic, crystalline powder.

α-Pyrocinchonylphenylhydrazine, $\begin{matrix}\text{MeC}\cdot\text{CO}\\ \parallel\\ \text{MeC}\cdot\text{CO}\end{matrix}\!>\!\text{N}\cdot\text{NHPh}$, is prepared by

mixing cooled ethereal solutions of pyrocinchonic chloride (1 mol.), prepared by the action of phosphoric chloride on pyrocinchonic anhydride and phenylhydrazine (3 mols.; compare Pickel, Abstr., 1886, 545). The precipitate thus obtained is washed with warm water and crystallised from dilute alcohol; it forms soft, yellow needles, melts at 187°, and is soluble in hot alcohol and benzene.

When phenylhydrazine (4 mols.) acts on α-dichloro-symmetrical-dimethylsuccinic anhydride (1 mol.), phenylhydrazine hydrochloride, nitrogen, benzene, and β-pyrocinchonylphenylhydrazine are formed. This reaction is remarkable, because Otto and Beckurts (Abstr., 1885, 753) could only obtain very little pyrocinchonic acid by the action of "molecular" silver on dichlorodimethylsuccinic acid.

α-Dichloropropionic anhydride, obtained by acting on the acid with phosphorus trichloride, is a colourless liquid boiling about 200°, of peculiar odour, and exciting a copious flow of tears.

A *propionylphenylhydrazine*, $CMe(N_2HPh){\cdot}CO{\cdot}NH{\cdot}NHPh$, is formed when phenylhydrazine (8 mols.) acts on α-dichloropropionic anhydride (1 mol.), a phenylhydrazine residue taking the place of both chlorine-atoms; it crystallises in nearly white, lustrous plates melting at 163°, and is soluble in hot water, alcohol, ether, and benzene.

A. G. B.

Coniceïnes. By E. LELLMANN (*Ber.*, **23**, 2141—2142).—All the three methods described by Hofmann (Abstr., 1885, 401) for the preparation of α-coniceïne yield different products. The base obtained by treating conhydrine with hydrochloric acid is probably α-coniceïne; the compound formed by the action of hydriodic acid on conhydrine the author names ϵ-coniceïne, and that obtained by treating bromoconiine with sulphuric acid, δ-coniceïne.

α-Coniceïne boils at 158°, is very hygroscopic, has a sp. gr. of 0·893, and forms a deliquescent hydrochloride; its picrate melts at 224° and its aurochloride at 196—198° with previous decomposition.

δ-Coniceïne boils at 158°, is not hygroscopic, and has a sp. gr. of 0·8976; it is lævo-rotatory (−7° 48′), and its *hydrochloride* is stable in the air. The *picrate* melts at 226°, and the *aurochloride* at 207° with slight decomposition; the *platinochloride* is moderately easily soluble.

ϵ-Coniceïne boils at 150—151° and is not hygroscopic; it is dextrorotatory (42°), and its *hydrochloride* is very deliquescent. The *picrate* melts at 223—224°, and the *aurochloride* at 176°, seemingly without decomposition; the platinochloride is very readily soluble.

F. S. K.

Strychnine. By H. BECKURTS (*Arch. Pharm.*, **228**, 313—325).—The strychnine employed, prepared from commercial nitrate, crystallised in anhydrous, four-sided prisms, which melted with blackening at 265°. If the temperature be raised quickly, the melting point appears to be considerably higher. Several analyses were made, the results agreeing best with the formula $C_{21}H_{22}N_2O_2$. Laurent (*Annalen*, **69**, 14) has shown that the action of bromine on an aqueous solution of strychnine hydrochloride converts it into bromostrychnine, which is precipitable by ammonia as a white, crystalline compound.

α-Monobromostrychnine, $C_{21}H_{21}BrN_2O_2$, is obtained by adding bromine (2 atoms) in the form of bromine-water to a solution of strychnine hydrobromide (1 mol.), and then precipitating with ammonia. By slow evaporation of the alcoholic solution of this precipitate, well-formed, rhombic plates are obtained which melt at 222°, and are only very slightly soluble in water, slightly soluble in ether, and easily in chloroform, benzene, and alcohol. The aqueous solution has an alkaline reaction and a very bitter, persistent taste. Its colourless solution in concentrated sulphuric acid gives a momentary, light-blue coloration on the addition of potassium dichromate. The aqueous solution gives precipitates with tannin, potassium mercury iodide, phosphotungstic acid, phosphomolybdic acid, potassium chromate, and platinum chloride. Monobromostrychnine hydrochloride, $C_{21}H_{21}BrN_2O_2,HCl$, and the corresponding hydrobromide, nitrate, and sulphate, the latter with 7 mols. H_2O, are easily obtained in crystalline forms.

α-Monobromostrychnine methiodide, $C_{21}H_{21}BrN_2O_2,MeI$, is obtained by warming an alcoholic solution of α-monobromostrychnine with excess of methyl iodide for several hours on the water-bath. The white, pearly, crystalline laminæ are sparingly soluble in alcohol, ether, chloroform, and water; on heating, they are charred without melting. The action of light turns them yellow, and they do not give the strychnine reaction with sulphuric acid and potassium dichromate. The corresponding *hydroxide*, $C_{21}H_{21}BrN_2O_2,MeOH + 4H_2O$, is obtained in slender, white needles on digesting the methiodide compound with excess of silver oxide for a short time on the water-bath, and filtering off the silver iodide formed; it chars at 260° without melting, is readily soluble in water and dilute alcohol, becomes yellow on exposure to light, and gives a very changeable, violet coloration with sulphuric acid and potassium dichromate.

Mononitrobromostrychnine, $C_{21}H_{20}(NO_2)BrN_2O_2$, is prepared by gradually adding 5 grams of monobromostrychnine nitrate dried at 105° to 50 grams of concentrated sulphuric acid cooled by a freezing mixture. After three days, the dark-yellow liquid is poured into 5 litres of water, and, after cooling, supersaturated with ammonia. The yellow, flocculent precipitate, recrystallised from alcohol, gives pale-yellow prisms, which on heating intumesce and coke, dissolve easily in acetone and dilute alcohol, but with difficulty in chloroform, benzene, and water. With sulphuric acid and potassium dichromate, the compound gives the strychnine reaction. The base does not give well-crystallised salts with acids. The hydrobromide and hydrochloride are yellow and amorphous. With platinic chloride, the base dissolved in hydrochloric acid gives a yellow, crystalline precipitate of the platinochloride, $[C_{21}H_{20}Br(NO_2)N_2O]_2,H_2PtCl_6$, which is sparingly soluble in alcohol.

Amidobromostrychnine, $C_{21}H_{20}Br(NH_2)N_2O_2$, is produced by heating a hydrochloric solution of the corresponding nitro-derivative for some hours with tin-foil on the water-bath; the dissolved tin is removed by hydrogen sulphide and the amido-compound precipitated by ammonia. On recrystallising from alcohol of sp. gr. 0·93, small, brownish needles are obtained. The compound is only slightly soluble in chloroform,

acetone, and ether; the solutions quickly decompose. It softens at 140° and melts at 180° to a brown liquid. The solutions in acidified water also quickly decompose. The yellow platinochloride soon becomes violet on exposure to air. J. T.

Brucine. By H. Beckurts (*Arch. Pharm.*, **228**, 326—330).—Laurent has described a monobromobrucine, but the author did not succeed in obtaining it by the method given. If bromine-water is added to an aqueous solution of brucine hydrobromide in the proportion of 2 atoms of bromine to 1 molecule of the salt, a precipitate appears which is first violet, then brown, and finally pure yellow; it has the formula $C_{23}H_{26}N_2O_4Br_3$. This compound dissolved in dilute alcohol, has an alkaline reaction; in the air it gradually forms an intense, red syrup. At 150° it evolves bromine, becoming brown, and at higher temperatures it chars. The aqueous solution of the compound has an acid reaction, and on concentration white or brownish plates of brucine hydrobromide, $C_{23}H_{26}N_2O_4,HBr + 3H_2O$, crystallise out. The mother liquor on evaporation gives a residue which appears to be dibromobrucine, $C_{23}H_{24}Br_2N_2O_4$. 10 grams of brucine treated with 200 grams of chlorine-water dissolved, but gave no crystalline product on evaporation; the deep-red, amorphous, dry residue, *dichlorobrucine*, $C_{23}H_{24}Cl_2N_2O_4$, is insoluble in ether, chloroform, benzene, and absolute alcohol. If a mixture of brucine and strychnine is treated with chlorine-water, the former goes into solution as dichlorobrucine, and the residue of strychnine salt will then give the strychnine reaction with sulphuric acid and potassium dichromate. J. T.

Stereochemistry of Nitrogen. By C. A. Bischoff (*Ber.*, **23**, 1967—1972).—It is generally assumed that in the case of a compound containing three radicles combined with a trivalent nitrogen-atom, no isomerides can exist. The author believes, however, that it is possible such isomerides may be found where the radicals combined with the nitrogen-atom become more complex, in which case, judging from his experience in the succinic acid group, the various isomerides would not so readily pass one into the other. He further points out that an isomeric methyldiphenylamine has already been described by Girard, Vogt, and Bardy, which Beilstein (*Handbuch*, **2**, 255), on account of the theoretical impossibility of an isomeric methyldiphenylamine, regards as phenyltoluidine. The physical constants of the compound do not agree well with this supposition, and a further investigation of the matter is therefore necessary.

A second group of nitrogen compounds in which isomerides may possibly exist, contains those in which the nitrogen-atom is combined with carbon by double or triple linkage. In this case, as already frequently stated, the isomerism is due to the fact that the mutual approximation of the doubly-linked atoms hinders the freedom of rotation. The third group, quite distinct from both the foregoing, is that of the hydroxylamine-derivatives.

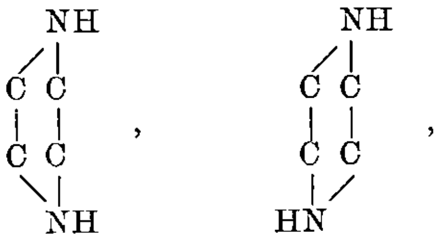
According to the author's ideas, the nitrogen-atom may be graphically represented in a similar manner to the carbon-tetrahedron by a quadratic pyramid; in its compounds, as, for instance, ammonium

chloride, the four hydrogen-atoms are situated at the four corners of the base, and the chlorine-atom at the apex. The direction of the valency at the apex makes, with that of each of the valencies at the base, an angle of 120°. In hydroxylamine, one atom of hydrogen is regarded as situated at the apex, and the remaining atoms of hydrogen and the oxygen-atom at the base. Isomerides can then be formed by the substitution of the hydrogen at the apex or one of those at the base by monovalent radicles. When, as in the case of the oximes, two hydrogen-atoms are replaced, three isomerides are possible, in which either both the hydrogen-atoms at the base are replaced, or the hydrogen-atom at the apex and one of those at the base. If the pentavalent nitrogen-atom passes into a trivalent atom, as when ammonium chloride loses hydrogen chloride, the three hydrogen-atoms rearrange themselves symmetrically, the directions of the three remaining valencies then forming with one another an angle of 120°.

H. G. C.

Stereochemical Studies in the Piperazine-group. By C. A. Bischoff (*Ber.*, **23**, 1972—1976).—The object of the researches of the author and his pupils on the mixed carbon and nitrogen rings is eventually to ascertain under what conditions the formation of closed chains of the general formula $A\cdot N<^{Cx}_{Cy}>N\cdot B$ takes place, A and B representing monovalent radicles, and x and y the number of carbon-atoms between the two nitrogen-atoms. In the present paper, only the case where $x = y = 2$ is discussed, that is, the formation of the members of the piperazine-group.

Starting with the assumption that the valencies of the carbon-atom make with one another an angle of 109° 28′, and those of the trivalent nitrogen-atom 120°, it is found that two spacial configurations of the piperazine skeleton are possible, namely :—



I. II.

the conditions of equilibrium being more favourable in the second case. The results given in some of the following abstracts appear to show that isomerides corresponding with these formulæ do exist. Moreover, it is found that the nature of the radicals A and B exerts an influence on the relative facility with which one form passes into the other, and also appears to determine whether ring-formation takes place or not. Thus, whilst ethylene-derivatives readily condense with all primary amido-bases to form piperazines, the propylene-derivatives do not behave in a similar manner, and orthotoluidine does not form a closed chain under circumstances in which paratoluidine and aniline readily do so.

The influence of the alkyl-groups may also be observed in the closed chains containing an oxygen-atom in the ring, especially as regards the ease with which they are attacked by potash.

The action of nitrous acid on the piperazines does not always take place in the same manner, compounds being formed which in some cases give Liebermann's reaction, and in others not, whilst in certain cases the action is chiefly an oxidising one. An important difference between the piperazine- and piperidine-derivatives is that, in the former, hydrogen is never removed by oxidation without oxygen being substituted for it. H. G. C.

Diphenylpiperazine. By C. A. BISCHOFF and C. TRAPESONZJANZ (*Ber.*, **23**, 1977—1981).—The preparation of diphenylpiperazine has already been described (Abstr., 1889, 1010). Nitrous acid acts on diparamethoxydiphenylpiperazine,

$$MeO\cdot C_6H_4\cdot N<{CH_2\cdot CH_2 \atop CH_2\cdot CH_2}>N\cdot C_6H_4\cdot OMe,$$

(*loc. cit.*) with formation of three compounds, the first of which crystallises in reddish-yellow needles melting at 150—155°, the second, in brownish-black needles melting at 155°, and the third, in red plates melting at 215—220°. The first two give Liebermann's reaction, but not the third.

When phenetidine hydrochloride (34 grams) is treated with ethylene bromide (18 grams), sodium carbonate (34 grams), and water (200 grams), besides diparaethoxydiphenylpiperazine, the secondary base, *ethylene diparaethoxydiphenyldiamine*,

$$C_2H_4(NH\cdot C_6H_4\cdot OEt)_2,$$

is obtained. It crystallises from a mixture of ether and alcohol in colourless plates melting at 98°, and on further treatment with ethylene bromide yields the above diparaethoxydiphenylpiperazine. This melts at 218—223°, and by the action of nitrous acid yields *mononitrosodiparaethoxydiphenylpiperazine*, $C_{20}H_{25}N_3O_3$, melting at 80°, and decomposing at 170°, and a compound, $C_{20}H_{24}N_4O_6$, which forms yellowish-red needles melting at 120—130°.

An attempt was made to obtain a piperazine from propylene bromide by the action of aniline and sodium carbonate, but without success. H. G. C.

Diphenyl-αγ- and αδ-diketopiperazines. By C. A. BISCHOFF and A. HAUSDÖRFER (*Ber.*, **23**, 1987—1991).—The phenylglycin required for the preparation of diphenyl-αγ-diketopiperazine was obtained by Hausdörfer's method (Abstr., 1889, 1013), which gives a better yield than that proposed by Rebuffat (*Gazzetta*, **20**, 122).

Diphenyl-αγ-diketopiperazine, $PhN<{CH_2\cdot CO \atop CO\cdot CH_2}>NPh$, is only acted on by the gaseous mixture of oxides of nitrogen evolved from arsenious oxide and nitric acid, the quantity of substance obtained being then only small and difficult to purify. By the oxidation of this piperazine, the authors obtained results agreeing exactly with those of Abenius (this vol., p. 525).

The compound obtained as a bye-product on heating ethoxyphenylglycin (Abstr., 1889, 1012) when heated with acetic anhydride gives a *diparaethoxyphenyldiketopiperazine*, which is not identical with the $\alpha\gamma$-compound previously obtained, and is probably the $\alpha\beta$-compound, $EtO\cdot C_6H_4\cdot N<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}>N\cdot C_6H_4\cdot OEt$. It forms colourless, lustrous tablets melting at 177—178°.

Diphenyl-$\alpha\beta$-diketopiperazine, $PhN<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}>NPh$, is acted on by nitrous acid with formation of a golden-yellow compound melting at 93°. It has the formula $C_{16}H_{14}N_2O_2$ or $C_{16}H_{12}N_2O_2$, and contains therefore no more nitrogen and oxygen than the original piperazine. It is at present undergoing further investigation. H. G. C.

Ortho- and Para-ditolylpiperazines and β-Dinaphthylpiperazine. By C. A. BISCHOFF and A. HAUSDÖRFER (*Ber.*, 23, 1981—1986).—*Orthoditolylpiperazine*, $C_6H_4Me\cdot N<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>N\cdot C_6H_4Me$, is obtained in the same manner as diphenylpiperazine, the yield in this case being the worst of any in the piperazine-group, ethyleneditolylamine being obtained as a bye-product in the reaction. Orthoditolylpiperazine melts at 169—171°, and yields on treatment with nitrogen trioxide in sulphuric acid solution a compound, $C_{18}H_{20}N_4O_4$ or $C_{18}H_{18}N_4O_4$, melting at 282°, which does not show Liebermann's reaction.

Paraditolylpiperazine is much more readily prepared than the ortho-compound, and is best crystallised from chloroform. It melts at 187°, and is converted by nitrous acid into a compound crystallising in red prisms and melting at 175°, which gives Liebermann's reaction.

β-Dinaphthylpiperazine, $C_{10}H_7\cdot N<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>N\cdot C_{10}H_7$, obtained from β-naphthylamine, sodium carbonate, and ethylene bromide, forms colourless crystals melting at 228°. As a bye-product, the compound *ethylenedi-β-naphthyldiamine*, $C_2H_4(NH\cdot C_{10}H_7)_2$, is obtained; this forms colourless, lustrous plates or needles which melt at 149—150°. H. G. C.

Hydrastine: a Correction. By M. HEIM (*Ber.*, 23, 2469).—The compound (m. p. 166—169°) obtained by Freund and Rosenberg (compare this vol., p. 533) from methylhydrastine methiodide by the action of alkalis, has the formula $C_{20}H_{22}O_9$, not $C_{20}H_{20}O_8$ as given. F. Schmidt prepared, by the same method, a compound of the formula $C_{20}H_{18}O_7$; the difference is possibly caused by the manner of drying, the one being done at ordinary temperatures, the other at 100°. J. B. T.

Conversion of Tropidine into Tropine. By A. LADENBURG (*Ber.*, 23, 2225; compare this vol., p. 1167).—Further experiments have shown that the base obtained by treating tropidine with hydrobromic acid in the cold is identical with tropine. F. S. K.

Physiological Chemistry.

Influence of Muscular Work, Hunger, and Temperature on the Exhalation of Carbonic Anhydride. By V. GRANDIS (*Chem. Centr.*, 1890, i, 1069; from *Arch. Italien de Biologie*, **12**).—Experiments with dogs gave the following results:—

1. More carbonic anhydride is exhaled during muscular work than when the animal is at rest, whatever the conditions as regards food are.

2. When both fasting and tired, the animals exhaled less carbonic anhydride than under normal conditions, although for the first few hours after work the amount exhaled was greater.

3. The weight of the animal decreases much more rapidly after exercise than when fasting, six hours' exercise causing as great a loss of weight as when the animal fasted for four days.

4. If, after a seven days' fast, the animal is fed with double the usual amount of food, it regains its weight in three or four days, but this cannot be accomplished with animal food only. The breathing is less rapid during fasting, as also is the heart's action, especially in a warm atmosphere. J. W. L.

Glycogen in the Liver and Muscles. By E. HERGENHAHN (*Zeit. Biol.*, **27**, 215—227).—The conclusions from seven series of experiments, which are given with full analytical details and charts of results, are the following:—

1. The liver glycogen dwindles in hens after six days' inanition to very small quantities (0·0 to 0·098 gram; compare Prausnitz, this vol., p. 810).

2. The muscle glycogen, on the other hand, after the same period, is still present in considerable amount, although varying between wide limits (0·053 to 1·58 grams).

3. At the end of the period of abstinence, the store of muscle glycogen in all the experiments preponderated.

4. On the administration of cane-sugar, the liver glycogen soon shows a great increase; the muscle glycogen shows no important rise until 12 hours after the feeding.

5. As is shown graphically by curves, about six hours after the administration of cane-sugar as food, the liver glycogen has increased so much that it equals in amount the muscle glycogen. Later on, its amount exceeds that in the muscles, the time when this occurs varying with the dose; for instance, with

10	grams of cane-sugar,	in 15	hours.
20	,,	,, 20	,,
30	,,	,, 26	,,

6. The maximum of the liver glycogen occurs earlier when the dose of sugar is small; for instance,

Quantity of cane-sugar given.	Maximum of liver-glycogen appeared in—	Average amount of the maximum.
10 grams	12 hours	1·625 grams
20 „	16 „	1·980 „
30 „	20 „	3·585 „

7. The maximum of the muscle glycogen is independent of the amount of sugar administered, and appears 12 to 24 hours after the food is given.

8. As a rule, the maximum of the liver glycogen is somewhat greater than that of the muscle glycogen, but both are proportional to the amount of cane-sugar given.

9. The difference of time in the occurrence of the two maxima is lessened by increasing the amount of cane-sugar given. It vanishes with a dose of 30 grams.

W. D. H.

Formation of Glycogen in Muscle with an Artificial Circulation. By E. Külz (*Zeit. Biol.*, **27**, 237—246).—Previous observers have stated that a liver freshly removed from the body continues to form glycogen from dextrose dissolved in blood artificially pumped through the organ. In the present research, similar experiments were made with the muscles of the lower extremities of dogs. These were, after the death of the animal, kept at the body temperature, and after an experiment lasting five or six hours were still found excitable and contractile when tested with an electric stimulus. A measured quantity of blood was pumped through each limb in some experiments, but that passed through one limb had a known quantity of dextrose or cane-sugar dissolved in it; at the end of the experiment the amounts of glycogen in each limb were estimated and compared with one another; the amount of sugar left in the blood was also estimated. In other experiments, the control limb was not subjected to an artificial circulation, but the glycogen in it was estimated immediately after death. In a third series of experiments, the estimations were made not for the entire limbs, but for individual muscles of the limbs. The third series is regarded as unsatisfactory; the corresponding muscles of the two sides were practically equal in so far as their glycogen was concerned, or if any difference at all occurred, the control muscle contained the more glycogen. The muscles, however, did not respond to the electric current, and so may be regarded as dead. Death does not occur so soon when the whole limb is left intact, and the results of experiments conducted on this plan are, therefore, regarded as more trustworthy. Here it was found (except in two instances where the differences are so small as to come within the limits of experimental errors) that the limb through which the blood containing sugar had been pumped contained the greater amount of glycogen. This is regarded as evidence that the muscles have in themselves the power of producing glycogen from sugar, and are not merely dependent on the liver for their supply of glycogen.

W. D. H.

Phloridzin Diabetes. By F. Moritz and W. Prausnitz (*Zeit. Biol.*, **27**, 81—118).—J. v. Mering (*Verhandl. d. V and VI Congress inn. Med.*, *Zeit. klin. Med.*, **14**, 405; **16**, 431) has discovered in phloridzin an agent by means of which diabetes can be artificially produced in animals. Phloridzin is a glucoside, which, by boiling with an acid, is decomposed, yielding a sugar phlorose, which is almost identical with dextrose, and phloretin, which, by the action of caustic alkali, is split into phloroglucinol and phloretic acid. The constitution of phloridzin is not known with certainty; phloretic acid, however, is the acid of an aromatic alcohol, and phloroglucinol is a trihydric aromatic alcohol or phenol. It is probable that phloridzin contains free aromatic hydroxyl-groups. It therefore was necessary in the course of the investigation to determine the amount of ethereal hydrogen sulphate in the urine in addition to the sugar. The results of these experiments and others bearing on the influence of the drug on metabolism and other points may be thus stated:—

The phloridzin used was pure; it yielded phloretin which crystallised in needles melting at 226—230°, thus differing from that originally described by Stas (*Annalen*, **30**, 200), which crystallised in plates melting at 180°. A simple reaction for phloridzin is the red colour produced on evaporating it with a few drops of a solution of vanillin in alcohol, and a little hydrochloric acid. Iron chloride gives a brown coloration with solution of phloridzin. Neither of these tests, however, can be used for its identification in fæces, as they are not characteristic. Phloridzin may be best detected and estimated by the yield of sugar produced after hydrolysis with sulphuric acid. The absorption of phloridzin in the alimentary canal appears to be rapid and complete. After feeding an animal on the drug in doses of 1 gram per kilo. of body weight, it is not recognisable in the fæces. For a space of two days on the average after the administration of the drug, the urine contains a substance which gives a brown coloration with ferric chloride. The urine also contains an increased quantity of ethereal hydrogen sulphates on the day of the dose, and the succeeding day; the increase is so marked that it is only explicable on the grounds that part of the phloridzin given is combined in the urine as a sulphate. The following table represents the result of an experiment on a dog, bearing out this statement:—

Date.	Sulphuric acid.			Remarks.
	As normal sulphate (*a*).	As ethereal sulphate (*b*).	*a* : *b*.	
24th Nov. .	0·69	0·14	1 : 0·2	Normal.
4th Dec. .	0·85	0·11	1 : 0·13	Normal.
6th Dec. .	0·21	0·41	1 : 2·0	6 gr. of phloridzin given.
7th Dec. .	0·66	0·22	1 : 0·34	

The excretion of phloridzin, and the accompanying glycosuria,

appears to be completed within the second day after its administration. The total quantity of sugar in the urine is far greater than can be accounted for by the phlorose derived from the drug itself; it is a form of sugar which completely disappears under the influence of yeast, and is thus dextrose, doubtless mixed with phlorose.

Phloretin also causes glycosuria, but not so markedly as does phloridzin. Phloroglucinol and phloretic acid do not produce this result. Phloridzin diabetes is analogous to the most severe form of human diabetes; it occurs whatever the diet may be: meat, carbohydrate, or fat, or mixtures of these, or when no food is given at all. The excretion of sugar begins about three hours after the drug has been given, rises quickly to a maximum, and as rapidly falls; this corresponds to the rate of absorption and excretion of the drug. The percentage sugar contents of the urine varies greatly. A minimum of 6 per cent. and a maximum of 13·5 per cent. were observed. It varies with the amount of phloridzin given, and also with the amount of food taken. In this latter particular an increase of meat in the diet produces a more marked effect than an increase of the carbohydrates; this is, probably, dependent on the slower absorption of starch. If one calculates the maximal amount of sugar theoretically possible from the food, after allowing for the carbon discharged as urea, it is found that the quantity of sugar in the urine is much less, but in the case of meat diet is greater than in the case of starchy foods. The output of sugar during hunger and during a fatty diet is very great, relatively much greater than when carbohydrates and meat are taken. The destructive metabolism of proteïds during an abundant meat diet is only slightly increased by phloridzin; this is very different from what occurs during inanition, then the nitrogenous output may be twice that of the normal; the increase is not so marked when fat is given as during absolute abstinence from food; carbohydrate food lessens the increase still more. W. D. H.

Phloridzin Diabetes. By E. Külz and A. E. Wright (*Zeit. Biol.*, **27**, 181—214).—J. v. Mering, in his researches on this subject (see preceding abstract), has administered phloridzin to animals after varying periods of inanition. He believes that these periods are sufficiently long to enable the animal to get rid of all its glycogen, and as the amount of sugar in the urine is greater than that derivable from the drug, concludes that the source of the sugar must in these cases be, for the greater part, the proteïds of the body. Although in his last published papers, v. Mering admits the presence of a small amount of glycogen in the animals killed after phloridzin poisoning, he does not consider that this is sufficient to cause him to alter his original conclusions. The present research, undertaken before the appearance of v. Mering's last paper, had for its chief object the ascertaining of the fact whether the animals, after long abstinence from food and dosing with phloridzin, are absolutely glycogen free. It was found that they were not; the quantity of glycogen, especially in the muscles, being so great as in the author's opinion to considerably invalidate v. Mering's position. A large number of

experiments on different species of animals are recorded with great fulness, and analytical details are succinctly tabled.

Minor points to be noted are the facts that phloretin (except in hens) causes diabetes, though not so powerfully as phloridzin; and that frogs do not suffer from glycosuria after the administration of either drug.

The paper concludes with some polemical remarks regarding the method of glycogen estimation used by v. Mering. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Silicic Acid as a Culture Medium for Organisms. By W. Kühne (*Zeit. Biol.*, **27**, 172—179).—Silicic acid prepared from water glass by the addition of hydrochloric acid, and dialysed until free from acid and sodium chloride, coagulates after a time, especially on the addition of sodium chloride. The solution found best for the purpose was one of sp. gr. 1·02, containing 3·4 per cent. of anhydrous silicic acid. After a few days, this sets to a clear, transparent jelly. This mixed with nutritive substances (meat extract, deuteroalbumose, &c.), and sterilised by heating in metallic vessels at 160—170°, is recommended as a culture medium for micro-organisms. W. D. H.

Occurrence of Boron in the Vegetable Kingdom and its Physiological Meaning. By E. Hotter (*Landw. Versuchs-Stat.*, **37**, 437—458).—A large number of ashes of fruits, leaves, and twigs of fruit trees and portions of other plants were tested for boron. 1 to 1·5 grams of the ash was dissolved in ·4 per cent. hydrochloric acid (10—15 c.c.) and tested with turmeric paper; if the result was uncertain or negative, a larger quantity of ash was tested with sulphuric acid and ethyl alcohol. Boric acid was found in the ashes of all the fruits which were examined; other ashes contained less.

In order to ascertain the physiological action of boron in plants, water-culture experiments were made with *Pisum sativum* and *Zea Maïs.* When much boron is taken up by the plant, the chlorophyll is destroyed, and consequently the process of assimilation stopped; and the root dies. When the amount of boron in the nutritive solution is increased, the plant becomes still less healthy; with 1 gram per litre the dry produce is very slight. Free boric acid is more prejudicial than the alkali salts. Different kinds of plants are differently affected by the same amount of boron; peas were much less able to resist its action than maize. The distribution of the boron was nearly equal in the healthy and unhealthy organs.

N. H. J. M.

Composition of the Ash of Tobacco Leaves. By J. M. van Bemmelen (*Land. Versuchs-Stat.*, **37**, 409—436).—According to Nessler, Schloesing, and others, tobacco will burn well which is rich

in organic potassium salts. Too much potassium nitrate is injurious; potassium chloride is also injurious, and calcium and magnesium chlorides still more so, owing to their fusibility and the consequent encasing of unburnt organic matter. Of organic substances, too much fat and too much albumin neutralise the good effect of organic potassium salts. It is of importance that the albuminoïds and carbohydrates should be sufficiently decomposed in the curing.

Ash analyses are given of tobacco from Java, Mexico, Japan, Hungary, and Virginia. The results show that leaves of the best quality contain 12 to 15 per cent. of mineral matter (silica excluded), not much chlorine and sulphuric acid, no soda, or very little, and much potash, lime, and magnesia in combination with organic acids; that in the ash, not only the relation between the carbonates and the chlorides and sulphates ($CO_2 : Cl + SO_3$) is high (not under 7), but also that the relation between the potash and chlorides and sulphates ($K : Cl + SO_3$) is not under 2.

Tobacco which burns badly either contains an excess of chlorine and sulphuric acid over the amount of potash, or else the amount of potassium, compared with that of chlorine and sulphuric acid, is low, owing to the potash being partially replaced by soda. It is important to determine how far lime may replace potash. The total amount of ash in the best tobacco of different countries varies only slightly, and as the amount of chlorine, sulphuric acid, and soda is small, it is not improbable that lime, magnesia, and potash, as organic salts, can replace one another within certain limits. N. H. J. M.

Loss of Nitrogen in Acid Fodders. By F. W. Woll (*Landw. Versuchs-Stat.*, **37**, 466—469).—A reply to Kellner and Sawano (this vol., p. 546). Although acid clover and other Leguminosæ lose nitrogen by dissociation of ammonium salts in drying, it has been shown that such a loss either does not take place at all, or is only very slight in the case of the acid fodders poorer in nitrogen, as for instance, green maize. In this case, the loss of nitrogen is due to the action of ferments. N. H. J. M.

Composition of Soils. By J. M. van Bemmelen (*Landw. Versuchs-Stat.*, **37**, 347—373; compare this vol., pp. 822, 823, 832).—In the soils examined by the author, namely, sea mud, arable land, and volcanic arable land (Sumatra and Java), it was found that the amount of humus in relation to that of the clay, was greatest in freshly deposited mud; the heavy clay contained 30 per cent. of silica and alumina, and 6·9 per cent. of humus; the lighter clay, 17 per cent. of silica, and 3·2 per cent. of humus. The percentage of nitrogen in humus varied from 4·5 to 7 per cent. The humus contains absorbed mineral matter, especially alkaline bases, which are of considerable importance for the fertility of the soil. The fertility of soil also depends on the state of humification of the organic matter. Pitsch's experiments (*Landw. Versuchs-Stat.*, **26**, 1) show that Grandeau's conclusions with regard to his so-called *matière noire* were erroneous.

The volcanic clay contained more colloïdal silicates than ordinary clay, and was also more readily decomposed by hydrochloric acid and

by dilute aqueous potash. Ordinary clay contains more silicates decomposable by sulphuric acid.

With regard to the alkaline bases in the colloïdal silicates and humates, it is suggested that the lime in the silicate is only in the most readily soluble portion; or else that dilute hydrochloric acid can extract lime from the colloïdal silicates without decomposing them. The amount of potash is greater in sea and river clay than in volcanic clay. The heavy sea clay contained 1 per cent. of potash; the lighter clay 0·4 per cent. Magnesia is less strongly combined in the colloïd silicates and humates than potash, but more strongly than lime.

The percentage of phosphoric acid (soluble in nitric acid) in manured or unmanured arable land is generally between 0·25 and 0·10, except when the soil contains much chalk or sand, when it may be only 0·05. N. H. J. M.

Causes of Fertility of the Forest-land of Deli (Sumatra) and Java for Tobacco, and of the Decrease of Fertility. By J. M. VAN BEMMELEN (*Landw. Versuchs-Stat.*, **37**, 374—408).—The causes of the fertility for tobacco of the volcanic clay of Deli are the fresh forest soil, its loose texture, the amount of humus it contains, and probably also the basic composition of the silicates. The frequency of rain during the period of growth of the tobacco plant is also favourable. The cause of decrease of fertillity, which does not seem to be due to exhaustion of the soil, requires investigation. The crops are still sufficiently large, but the quality of the leaves is inferior. It is suggested that the composition of the humus has changed, and that the soil has lost its looseness of texture. The author suggests that the fertility might be restored by occasionally re-establishing the forests for a time. N. H. J. M.

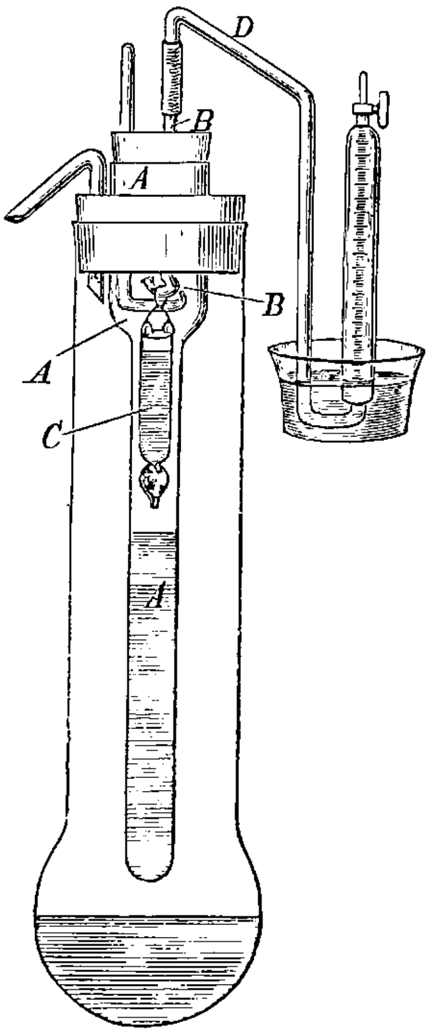
Loss of Nitrogen during the Fermentation of Nitrogenous Organic Matters and the Means for its Prevention. By H. v. KRAUSE (*Chem. Centr.*, 1890, i, 1065—1066; from *Journ. Landwirthschaft*, **38**, 1–68).—The decomposition and loss of nitrogen sustained by cow-dung was investigated, and the effect of the addition of several substances was determined. Superphosphate added in quantities of from 0·5 to 5·0 per 100 of the dung, proved to be an excellent means of preventing decomposition. Similar quantities of "superphosphate-gypsum" appear to assist rather than to retard the decomposition, but it nevertheless possesses considerable retentive power for ammonia.

Additions of kainite, from 0·5 to 15·0 per 100 of dung, assisted materially in preventing loss of ammonia when the dung was allowed to lie for short periods of time only; when kept in heap for protracted periods, considerable losses of ammonia, however, took place. Peat, when used in quantities from 0·5 to 10·0 per 100 of the dung, assists the decomposition, and considerable loss of nitrogen occurred. When added in much larger quantities, its power of absorbing ammonia becomes of value, and is useful where the urine is allowed to remain with the solid excrements. The addition of "basic phos-

phate" assisted the fermentations, and a very considerable loss of ammonia occurred. Lastly, experiment showed the importance of keeping the air from the dung, and that consequently less loss of ammonia occurs in the case of the dung being allowed to accumulate in the stalls than when it is regularly removed to a separate dung-heap. J. W. L.

Analytical Chemistry.

Apparatus for the Estimation of Nitrogen in Ammonium Salts. By W. Hentschel (*Ber.*, **23**, 2402—2403).—The method is based on the decomposition of ammonium salts by sodium hypobromite. The apparatus consists of an outer vessel similar to those employed in V. Meyer's vapour-density apparatus; it contains a small quantity of methyl alcohol, and is closed by a rubber stopper,



through this passes a short bent tube, the ends of which are cut at an acute angle. The inner vessel AA contains the sodium hypobromite solution, and is closed by a doubly bored rubber stopper. The delivery tube BB is bent at one end into a hook, on which is suspended, by a piece of platinum wire, the tube C; this tube contains a little mercury and a weighed quantity of the ammonium compound under examination. Through the second hole of the stopper, a bent glass rod passes easily, so that it may be freely turned. D is a capillary tube. The details of working are as follows:—The apparatus is heated by boiling the alcohol for about half an hour; when bubbles cease to appear at D, the tube C is released by means of the bent rod, and allowed to drop into the liquid in AA. An immediate evolution of nitrogen takes place, which displaces an equal volume ot air; the reaction is completed in a few minutes. No special correction is needed in measuring the mixture of air and nitrogen.

J. B. T.

Source of Error in the Estimation of Sulphuric Acid. By E. v. MEYER (*J. pr. Chem.* [2], **42**, 270).—The author points out that in the evaporation of large quantities of liquids on the water-bath, a not inappreciable amount of sulphuric acid may be absorbed from the gases given off by the combustion of the coal-gas used for heating, which is never free from sulphur. Experiments made with distilled water free from sulphuric acid showed that in evaporating 2 litres in a porcelain basin to 50 c.c. (which occupied six hours), an amount of sulphuric acid equal to 0·01462 gram SO_3 was absorbed. In another experiment 1 litre of pure water was evaporated in a platinum basin over a small Bunsen flame to 50 c.c. (the time occupied being 12 hours); in this case the amount of sulphuric acid found corresponded with 0·0106 gram SO_3.

H. G. C.

Oxidation of Sulphides by the Electric Current. By E. F. SMITH (*Ber.*, **23**, 2276—2283).—The substance to be examined was fused with caustic potash in a nickel crucible, which was connected with one end of an electric circuit, whilst a platinum wire dipping into the fused mass was connected with the other. In the circuit were also interposed an ammeter, for measuring the strength of the current, an apparatus for reversing the direction of the current, and a variable resistance. Rather more than 0·1 gram of the substance was generally used with 20—40 grams of caustic potash, and the current was allowed to run for 10 to 20 minutes, at a strength of 1—2 ampères; it was often found advantageous to reverse the current occasionally. The crucible and its contents were finally treated with water, the solution filtered from insoluble oxide, acidified, and the sulphuric acid in it estimated in the usual manner. It was found that in the case of blende, ZnS; cinnabar, HgS; galena, PbS; silver-glance, Ag_2S; molybdenum-glance, MoS_2; stibnite, Sb_2S_3; orpiment, As_2S_3; jamesonite, $Sb_2S_5Pb_2$; enargite, AsS_4Cu_3; stephanite, $Sb_2S_8Ag_{10}$; kobellite, $(BiSb)_2S_5Pb_2$; fahlerz, $(SbAs)_2S_7(Cu_2Hg_2FeZn)_4$; tin pyrites, SnS_4Cu_2Fe; pyrrhotite, $Fe_{11}S_{12}$; and marcasite, FeS_2, all the sulphur was oxidised to sulphuric acid by treatment in the manner described above, but not more than half the sulphur in copper-glance,

Cu_2S, could be thus oxidised, while to effect the complete oxidation of iron pyrites, FeS_2, it was found necessary to add an equal weight of copper oxide, and use a current of 4 ampères. C. F. B.

Blowpipe Test for Mercury. By T. CHARLTON (*Chem. News*, **62**, 41—42).—After the sublimate is obtained in Johnstone's method for testing for mercury (Abstr., 1889, 797), the author recommends dropping a little iodine into the tube; when volatilised, this immediately gives the characteristic mercuric iodide if any mercury is present, whilst the inconvenience caused by the washing away of sublimate by the use of acid is obviated. D. A. L.

Reactions of Arsenic. By G. LOOF (*Chem. Centr.*, 1890, i, 1078—1079; from *Apotheker Zeitung*, **5**, 263).—The author recommends hypophosphorous acid as the best reagent for arsenic, as described by J. Thiele (this vol., p. 1193). Arsenic is only precipitated from the strongly hydrochloric acid solution by heating. 10 c.c. of hydrochloric acid, if heated for several hours with 0·1—0·2 gram of calcium hypophosphite, will show the presence of arsenious oxide if 0·01 milligram be present. Of glycerol, sulphuric acid, phosphoric acid, 5 c.c. with 10 c.c. of concentrated hydrochloric acid is a suitable quantity; of calcium phosphate, sodium phosphate, or tartar emetic, 0·5 gram in 10 c.c. of hydrochloric acid, is sufficient. In the case of bismuth subnitrate, it should be previously freed from nitric acid by gentle heating, or by dissolving an equal weight of the hypophosphite with it in hydrochloric acid. Of *liq. ferri sesq.* 5 c.c. in 10 c.c. of hydrochloric acid is decolorised with Bettendorf's reagent, and then 0·2 gram of the hypophosphite added. Antimony oxysulphide is dissolved by hydrochloric acid and potassium chlorate, filtered through glass wool, and heated with hypophosphite for several hours on the water-bath. J. W. L.

Quantitative Estimation of Vanadium and the Separation of Vanadic Acid from Phosphoric Acid. By R. HOLVERSCHEIT (*Inaugural Dissertation*, *Chem. Centr.*, 1890, i, 977—978).—By the application of Rosenheim's iodometric method (*Annalen*, **251**, 197), the author finds that vanadic acid may be rapidly and exactly determined, after first precipitating it as barium or lead vanadate. The substance is dissolved, and the vanadic acid precipitated with barium chloride or lead acetate. The precipitate is boiled with hydrochloric acid and potassium bromide, and the liberated bromine determined volumetrically with potassium iodide. In the absence of substances, such as molybdic acid, which are reduced by sulphurous acid or hydrogen sulphide, the vanadic acid may also be determined by first reducing it with one of these agents, the excess being then boiled off, and the vanadium tetroxide determined by potassium permanganate. If the vanadic acid has been precipitated as barium or lead vanadate, the metal must first be separated before titrating with potassium permanganate. For the determination of vanadic acid and phosphoric acid when they occur together, the vanadic acid is first reduced to tetroxide with sulphurous acid, and after expelling the excess of the

latter, the phosphoric acid may be precipitated with molybdic acid and filtered off. If the amount of vanadic acid is large, the precipitation of the phosphoric acid should be executed rapidly at 55—60°, using a considerable excess of molybdic acid; or the vanadic acid may first be determined in the solution by boiling with hydrochloric acid and potassium bromide, the liberated bromine being then determined volumetrically; the phosphoric acid is determined by evaporating the solution with a little sulphuric acid to dryness, the residue is taken up with water, the vanadic acid reduced with sulphurous acid, and the phosphoric acid precipitated with molybdic acid, as above described. If the alkalis are to be determined, the substance, dissolved in acetic acid, is treated, at boiling heat, with lead acetate, and the lead vanadate filtered off, the alkalis being then determined in the filtrate. J. W. L.

Detection and Estimation of Lactic and Butyric Acids in Wines. By E. MACH and K. PORTELE (*Landw. Versuchs-Stat.*, **37**, 305—323).—Owing to heavy rainfalls and consequent flooding of wine-districts in South Tyrol, the grapes often become covered with a thin crust of mud. This contains, besides clay, a considerable amount of calcium and magnesium carbonates, which neutralise much of the acid of the grapes, and give rise to lactic and butyric fermentation. The resulting wine blackened when exposed to air, and could only be used for making inferior brandy. The mud-crust may, however, be almost entirely removed by immersing the grapes for a few minutes in 2 or 3 per cent. sulphuric acid; they are afterwards washed in running water. Determinations of alcohol, total acid, volatile acids, potassium hydrogen tartrate, glycerol, ash, and ash constituents were made at different periods, in samples of wine prepared (*a*) after washing the grapes with acid; (*b*) without washing the grapes, and letting the must ferment with the skins; (*c*) same as (*b*), but the must was drawn off, allowed to settle, and again drawn off; (*d*) same as (*c*), but the must was treated with sulphuric acid (1·83 grams per litre). The results of the analyses are given in tables. Acetic, butyric, and lactic acids were determined in samples (*a*), (*b*), and (*c*). The results show that the wine prepared from the grapes washed with acid was free from butyric and lactic acids, whilst the greater part of the small amount of acid in (*b*) consists of lactic acid.

Detection and Estimation of Butyric Acid in Presence of Acetic Acid. —500 c.c. of wine is distilled until 125 c.c. remains; the residue is diluted to its original bulk, and again distilled until 125 c.c. remains. This is repeated four times, and the free acid in the united distillates determined by titration with soda or with baryta. If soda has been used, the neutralised distillate is evaporated down, treated with dilute sulphuric acid, and steam distilled, and the distillate neutralised with baryta. The solution is so far evaporated down that it will solidify when cold, after which it is treated with absolute alcohol (10 parts). The barium butyrate dissolves, whilst the acetate remains almost entirely undissolved. The salts are separated by filtration and washing with absolute alcohol. The aqueous solutions of the salts are treated with sulphuric acid, steam distilled, and the acid determined by titra-

tion with soda. In order to ascertain whether the separation was complete, the neutralised solutions are evaporated down and treated with alcohol and sulphuric acid; a trace of impurity is easily detected by the odour of ethyl salt.

Detection and Estimation of Lactic Acid.—500 c.c. of wine is just neutralised with soda, some pumice powder added, and the whole evaporated to dryness in a deep dish on a water-bath, with frequent stirring. The residue is rubbed in a mortar, moistened with dilute sulphuric acid, and shaken three times with ether (200 c.c.). The united ether extracts are carefully evaporated down in an Erlenmeyer flask, the residue washed with water into a deep dish, treated with an equal volume of alcohol, and slightly heated for a long time with freshly precipitated lead carbonate, until effervescence ceases. It is then digested for three or four hours, filtered, and washed with 95 per cent. alcohol. The filtrate is decomposed by hydrogen sulphide, filtered, heated on a water-bath to remove excess of hydrogen sulphide, and distilled until one quarter remains. It is then diluted to its original bulk and again distilled, and this is repeated until the distillate is neutralised by not more than 0·5 c.c. of normal soda solution. The lactic acid in the residue is determined by titration. The results thus obtained are too high, owing to the presence of malic acid. The neutralised solution is therefore evaporated to dryness, and the sodium lactate dissolved out by absolute alcohol (sodium malate being insoluble). After evaporation of the alcohol, the residue is treated with dilute sulphuric acid, and extracted three times with ether. The residue from the ether is digested with lead carbonate, and the acid afterwards liberated as before. The solution of acid is divided into two parts, the one being used for the titration, and the other converted into zinc salt, to determine its purity.

Palm's method (Abstr., 1887, 307) was tried, and although it answered well for the detection of lactic acid, it was found to be unsatisfactory as a quantitative method. N. H. J. M.

Quantitative Estimation of Uric Acid in Human Urine. By W. Camerer (*Zeit. Biol.*, **27**, 153—171).—The method adopted for the estimation of uric acid consists in estimating the nitrogen in the precipitate of uric acid produced by silver nitrate (Abstr., 1889, 1040); Salkowski and after him Ludwig, however, decompose the precipitate produced by silver nitrate with sulphuretted hydrogen or sodium sulphide and weigh the uric acid as such. Camerer's simpler method has certain disadvantages. Some authors have stated that a loss of uric acid is unavoidable; this is found to be more marked in urines than in solutions of pure uric acid; it is independent of the concentration, and is apparently due to imperfect filtering; it was found that the error was so small as to be negligible, if Schleicher and Schull's filters were used. Another objection is that silver nitrate precipitates from urine not only uric acid, but certain substances of the xanthine group. A number of comparative experiments were therefore made, the uric acid being estimated both by the author's method and by Ludwig's method. The latter was found to be by no means a simple process, and the difficulties are

pointed out and improvements in the methods of filtration, &c., suggested. The results in two analyses by the two methods were identical; in the remaining nineteen analyses, Ludwig's method gave the lower result, the percentage difference varying from 5·9 to 16·7, the mean being 10·9. In order to avoid the lengthy and troublesome method proposed by Ludwig, it is recommended that the quantity of uric acid present be calculated from the quantity as found by the author's method, as in the following example: The silver precipitate of 150 c.c. of the diluted urine yielded 14·39 milligrams of nitrogen, or 9·6 per 100 c.c. $9·6 \times 3 = 28·8 =$ the quantity of uric acid by Camerer's method. The quantity found by Ludwig's method was 26·0. Taking the mean percentage difference as 11 instead of 10·9, the true amount of uric acid can be calculated from Camerer's number, thus—$28·10 - (28·8 \times 0·11) = 25·6$, which is nearly the same number as that obtained by direct analysis. If several analyses be made, and the mean taken, the results as shown in a table are practically identical in those obtained by calculation and by experiment.

The physiological deductions from the experiments recorded coincide very closely with those of Schultze (this vol., p. 280), the following being the average numbers obtained from patients suffering from gout:—

Diet.	Urea nitrogen.	Uric acid nitrogen.	Total nitrogen.	Uric acid nitrogen.
Mixed diet with alcohol.	100	2·36	100	1·5
Mixed diet with mineral water instead of alcohol	100	1·9	100	1·2

Some analyses are also given of the urine from three patients suffering from febrile complaints; the most marked point noted appears to be the large quantity of xanthine compounds excreted; that is the difference in the uric acid by Ludwig's method, and that by the author's method is greater than the normal mean.

W. D. H.

Estimation of Fat in Milk in Dairies. By O. LANGKOPF (*Chem. Centr.*, 1890, i, 981—982; from *Pharm. Zeit.*, **35**, 225).—The author recommends the Soxhlet's method by means of the areometer, and that of de Laval by means of the lactocrite. The latter is carried out as follows: 10 c.c. of milk is heated with 10 c.c. of a mixture of acetic acid (95 vols.) and sulphuric acid (5 vols.) in a test tube on the water-bath for 7—8 minutes. The test tube is closed by an india-rubber stopper carrying a glass tube 20 cm. long. By this means the caseïn is completely dissolved and the fat floats to the surface. The whole of the contents of the test tube are transferred to a small metal capsule, into which is then pushed a glass tube, so wide at the base that it exactly fits into the capsule, the liquid contents being thus forced up into the glass tube. The latter is thick walled, having but a narrow bore, and the column of liquid

thus becomes a long one; it is also graduated in such a manner that each division is equivalent to one-tenth per cent. of butter fat. For the better separation of the separated fat, these tubes are fixed into a centrifugal apparatus, which is worked for ten minutes at a rate of 6000—7000 revolutions per minute. J. W. L.

Examination of Oils, Fats, &c. By T. T. P. B. Warren (*Chem. News.*, **62**, 27—28, 51, and 75).—These substances may, according to the author, be divided into three classes as regards their behaviour with sulphur chloride:—Those which are not acted on, those which yield a magma completely soluble in carbon bisulphide, and those which yield a magma only partially soluble in that solvent. When the sulphur chloride acts, hydrogen chloride is evolved, and the sulphur combines with the oil residue.

Animal, fish, and solid vegetable oils and fats, and also the fatty acids of fluid vegetable oils, do not yield products with sulphur chloride insoluble in carbon bisulphide, but the fluid vegetable oils do, and therefore the latter can be readily separated from the former by this means. The proportion of insoluble magma produced from a fluid vegetable oil is reduced by oxidation and therefore by treatment with ozonised air, or by keeping in air, or by hot pressing as compared with cold extraction, &c. Therefore the more readily oxidisable oils can be separated from the less readily oxidisable oils by treatment first with ozonised air, then with sulphur chloride, then with carbon bisulphide. Olive oil is the most stable oil as regards oxidation; whilst oils such as poppy, walnut, linseed, rape, and cotton oil oxidise rapidly, with the result (besides the diminution in the amount of the insoluble magma) that their viscosity is increased and their iodine absorption reduced, which may be estimated and taken as a measure of the oxidation. Sulphur chloride has comparatively little effect either on the weight or on the iodine absorption of the indifferent oil and fats. The total weight of magma should be ascertained in all cases.

As an example of a separation on the author's plan:—An olive oil adulterated with lard and cotton-seed oil would, after treatment with sulphur chloride, yield the lard oil to carbon bisulphide; but both the lard oil and the altered cotton-seed oil would be removed by this solvent by treating the adulterated olive oil first with ozonised air and then with sulphur chloride. Lubricating lard oil compounded of animal fat and cotton-seed oil, or of cotton-seed stearin and animal fat, or oleomargarin adulterated with cotton-seed oleïn, can be separated and detected. The action of sulphur chloride on the oils attacked by it is modified in mixtures of such oils, inasmuch as the more susceptible oil interferes with the action on the other; in mixtures of castor and rape oils for instance, the former absorbs most of the sulphur chloride, leaving much of the latter oil unattacked. The author points out that the oleïc and stearic acids separated from oils, &c., behaving differently with sulphur chloride, when reconverted into glycerides, yield products having the same distinctive characteristics as the original oils or fats; which seems to indicate a chemical difference in these oleïc and stearic acids.

Iodine tests must be made with great uniformity, should proceed for 24 hours at the same temperature in a warm dark room with precautions against the escape of iodine or other volatile matter. Hubl's reagent is most safely made up as required. D. A. L.

Colorimetric Method for Estimating Tannin in Barks. By S. J. HINSDALE (*Chem. News*, **62**, 19).—Material containing 1·5 to 10 per cent. of tannin is used in quantities of 0·8 gram per 500 c.c. of water, and five drops of the extract is treated with 5 c.c. of a mixture of 0·04 gram potassium ferricyanide and 1·5 c.c. of *liquor ferri chloridi* solution in 500 c.c. of water; after a minute, 20 c.c. of water is added, and within three minutes the colour is compared with that produced simultaneously and under exactly similar circumstances from a definite number of drops of a standard solution containing 0·04 gram of pure tannin in 500 c.c. of water; then the number of drops of the standard producing the same shade, correspond with the percentage of tannin present in the material. To avoid extremes in shades, extracts of materials containing more than 10 per cent. are made more dilute, and those with less than 1·5 per cent. stronger.

D. A. L.

Estimation of Tannin by means of Iodine. By A. MOULLADE (*J. Pharm.* [5], **22**, 153—159).—Carbon bisulphide is used as indicator in place of starch, and it is necessary to standardise the solution of iodine, and to make the assays under similar conditions. The iodine solution may contain 5·20 grams of iodine and 7·6 grams of potassium iodide per litre; this is standardised by means of a recently-prepared solution of pure and dry tannin, 1·0 : 1000 water; a 10 per cent. solution of hydrogen sodium carbonate is also required. 10 c.c. of tannin solution, about 20 c.c. of the sodium carbonate solution, 10 c.c. of water, and 2 to 3 c.c. of carbon bisulphide are placed in a flask and iodine solution is run in until the last drop gives a violet or rose tint to the bisulphide. If 10·5 c.c. of iodine has been used, a second assay is made, in which 10 c.c. is run in at once; if this is not sufficient, a third assay is made, running in 10·3 c.c., which gives the colour, say; then a fourth assay, using 10·2 c.c., and giving no colour, indicates that 10·3 c.c. of iodine measures 10 c.c. of the tannin solution. The astringent substances to be assayed are treated in the same way, and their contents in astringent acids can be expressed in terms of pure tannin. The assay should not contain more than 1·5 grams of tannin per litre. To 10 c.c. of the solution, 30 c.c. of the sodium carbonate solution is added, the 10 c.c. in excess being employed to largely saturate the astringent acids present, and the titration is made directly without filtration. To ascertain the real amount of tannin in a solution, the assay is repeated on another portion from which the tannin has been removed by treatment with skin. The method is applicable to all astringent substances, even to wine. In the case of wine, all interfering compounds are practically eliminated as follows:—The assay is first made on 10 c.c. of the wine; then 50 c.c. of the wine is mixed with 50 c.c. of a solution of gelatin (1 : 1000), and 20 c.c. of the filtrate is taken for a new assay. The difference between the volumes of iodine required in the two cases measures the tannin in the wine. J. T.

Colorimetric Method for Estimating Morphine in Opium Preparations. By S. J. HINSDALE (*Chem. News*, **62**, 77—78).—Various dilutions of officinal opium tincture with alcohol, 3 : 1, 2 : 2, 1 : 3, are prepared, and a single drop of each is treated with about 5 c.c. of fresh ferricyanide mixture (0·04 gram of potassium ferricyanide, 1·5 c.c. of *liquor ferri chloridi*, 500 c.c. of water), in about a minute 15 or 20 c.c. of water is added, and the colour observed; for examination, opium preparations are treated in a similar manner, and the shade produced compared with the standard. D. A. L.

Determination of Morphine in Opium. By G. LOOF (*Chem. Centr.*, 1890, i, 1082; from *Apotheker Zeitung*, **5**, 271).—The author recommends the following method:—5 grams of the finely-ground opium is carefully rubbed with water and diluted to 78 c.c. At the end of 1 to 2 hours, during which the mixture is shaken frequently, 60·8 c.c., corresponding with 4 grams opium, is filtered off, 0·2 gram of oxalic acid is added, and at the end of half-an-hour, 5·2 c.c. of potash (1 : 2) is added, the mixture well shaken, and 16·5 c.c. filtered through a dry filter into an Erlenmeyer flask of 30 c.c. capacity, this quantity corresponding with 1 gram of opium, 5 grams of ether, free from alcohol, is added, and the mixture shaken briskly for 10 minutes in the closed flask. The excess of ether is volatilised by blowing a current of air into the flask, after which the separated morphine is collected on a filter, and washed with water saturated with ether. The morphine on the dried filter may be transferred back to the portion remaining in the flask, and the weight of the whole obtained by drying until the weight of the flask and contents is constant. In the case of tincture of opium, 50 c.c. is used for each experiment, and of opium extract 2·5 grams is a suitable quantity, the remaining operations being the same as above described. J. W. L.

Testing Acetanilide. By E. RITSERT (*J. Pharm.* [5], **22**, 21—23; from *Pharm. Zeit.*, **35**, 306).—After drying for two hours at 105°, the melting point should be 114°. This may be raised or lowered by the presence of acetotoluidides. The following are tests for pure acetanilide:—0·1 gram is boiled by portions in 2 c.c. of concentrated hydrochloric acid; after cooling and the addition of one or two drops of chlorine-water, the liquid takes a beautiful blue tint. The aqueous solution of acetanilide should not have an acid reaction; on boiling the solution and adding a few drops of ferric chloride solution, a deep reddish-brown colour should be produced; this disappears on adding a mineral acid. If to a boiling aqueous solution of acetanilide (1 : 30) a drop of potassium permanganate solution (0·1 : 100) is added, the rose colour ought to persist five minutes at least, and should not become yellow on boiling afresh. Finally, the acetanilide should leave no solid residue when heated to redness. J. T.

Estimation of Pyridine Bases in Gas-liquor. By W. KINZEL (*Chem. Centr.*, 1890, i, 946; from *Pharm. Centralhalle*, **31**, 239—242).—The author bases his method on the fact that pyridine mercuric chloride is completely decomposed into pyridine and mercuric chloride

by boiling the aqueous solution for some time, the pyridine being precipitated. The mercurammonium chloride which, in the case of gas-liquors, would be formed at the same time is much more stable, becoming slowly converted into basic mercury compounds and ammonium chloride. J. W. L.

New Reactions of Albumins. By C. Reichl (*Monatsh.*, **11**, 155—165).—The author has previously (Abstr., 1889, 1092) called attention to the colour reactions obtained by treating the albuminoïds with alcoholic benzaldehyde or salicylaldehyde in presence of dilute sulphuric acid and ferric sulphate, and has now elaborated his previous experiments and extended them to other aromatic aldehydes.

Reaction with Benzaldehyde.—The blue condensation-product obtained on mixing egg-albumin, benzaldehyde, dilute sulphuric acid, and ferric sulphate, gives an absorption-band in the spectrum near D; apparently it is a compound of a base with sulphuric acid, for, on adding an alkali to the solution, the blue colour disappears with formation of a brownish-white precipitate, which dissolves in acids, again forming a blue or bluish-green solution. The precipitate dissolves in alkalis, yielding a yellow solution. The ferric sulphate plays the part of an oxidising agent, since dilute nitric acid, mercuric oxide, and other substances which readily part with their oxygen, may be substituted for it. This reaction of albumin appears to be due to the scatole-group contained in it, since scatole itself gives a bluish-violet coloration when similarly treated.

Reaction with Salicylaldehyde.—When the solid albuminoïd is moistened with a 0·5 per cent. alcoholic solution of salicylaldehyde, the alcohol allowed to evaporate, and the substance treated with a little dilute sulphuric acid containing ferric sulphate, coloured products are formed. Egg-albumin and blood-albumin, blood-fibrin, and caseïn give a bluish-violet; legumin, a brownish-violet; vegetable fibrin, a brownish-yellow; and sheep's-wool and skin, violet-blue compounds. After some time, the solid mass dissolves, forming a solution having the same colour. The bluish-violet solution obtained from egg-albumin shows an absorption-band in the spectrum between C and D, and contains a base which may be precipitated by alkalis. In order to recognise albumin in solution by this test, the liquid is mixed with a drop of the alcoholic solution of the aldehyde, an equal volume of concentrated sulphuric acid added, cooled, without shaking, and finally a few drops of ferric sulphate are poured in. According to the strength of the solution, a blue or violet zone is sooner or later formed. Salicylaldehyde gives a similar blue or violet solution when treated with scatole. The oil from *Spiræa ulmaria* gives the same reactions with the albuminoïds as salicylaldehyde, but the colour is not so intense.

Reaction with Anisaldehyde.—Egg-albumin, vegetable-albumin and caseïn give a violet coloration; blood-albumin and sheep's-wool, a violet-red; blood-fibrin, a blue; legumin, a brownish-violet coloration. The violet solution from egg-albumin gives an absorption-band between D and F. Alkalis precipitate a base which is apparently a scatole compound.

Reaction with Vanillin, Piperonal, Cinnamaldehyde, and Furfuraldehyde.—All these substances give coloured products with the albuminoïds and similarly coloured products with scatole.

The aromatic aldehydes, in presence of sulphuric acid and ferric sulphate, give coloured condensation-products with phenols, but these have an acid character, and unite with bases to form new coloured compounds. It consequently follows that in albumin it is the scatole-group which furnishes the coloured compounds above described. The production of these substances forms not only a very delicate test for albumin, but may be used conversely as a test for the presence of aldehydic compounds in wood, in resins, and in ethereal oils. G. T. M.

Analysis of Peptones. By G. Bruylants (*Chem. Centr.*, 1890, i, 1084; from *Revue Internal. Scientif.*, **3**, 167).—*Insoluble nitrogenous substances:* 6 grams of the substance is treated with water, diluted to 500 c.c., allowed to settle for two days, the clear liquid decanted, the insoluble portion washed by decantation, and weighed on a tared filter after drying at 105°. *Coagulable albumin:* 10 grams of the substance is treated with 300 c.c. of water, and, after clearing, 150 c.c. is filtered off and heated to boiling. The precipitated albumin is washed by decantation and weighed on a tared filter, after drying at 105°. *Albumose:* 5 grams of the substance is boiled in 200 c.c. of water, filtered, and 100 c.c. of the filtrate is evaporated to about 10 c.c. and 100 c.c. of a saturated solution of ammonium sulphate added. The precipitate obtained is washed with a cold saturated solution of ammonium sulphate, transferred to a tared filter, dried at 105°, and weighed. The adhering ammonium sulphate is then washed off with 500 c.c. of water, its amount determined by an estimation of the sulphuric acid, and the amount of precipitated albumin thus obtained by difference. For the nitrogen determinations, Kjeldahl's method is employed.

J. W. L.

Analysis of Peptones. By A. Denayer (*Chem. Centr.*, 1890, i, 1084—1085; from *Revue Internal. Scientif.*, **3**, 168).—The author considers the method of precipitating the albumose-peptone, as recommended by G. Bruylants (preceding abstract), inaccurate, since mucilage is precipitated by ammonium sulphate solution. He recommends the following method for the complete analysis of peptones:—*Mucilage:* 1—2 grams of peptone is treated with water and precipitated with Mayer's potassium mercury iodide solution (49·801 grams potassium iodide, 13·546 grams mercuric chloride, 1000 c.c. water), filtered, washed, concentrated to a few c.c., saturated solution of ammonium sulphate added, and the mixture heated to boiling, whereby the mucilage is precipitated. The precipitate is washed by decantation, then with ammonium sulphate, and, lastly, rapidly with cold water; the double iodide is separated with boiling alcohol, and the mucilage, with adhering ammonium sulphate, is weighed. The ammonium sulphate is determined, and its weight deducted. *Albumose peptone:* 1—2 grams of peptone is treated with 5 c.c. of water,

the mucilage and albumose precipitated with ammonium sulphate, and the precipitate weighed, from which is deducted the weight of mucilage and ammonium sulphate. *Peptone:* 1—2 grams of substance is dried in a vacuum at 60°, whereby the substance swells up, and is then washed with 95 per cent. alcohol. The residue is dissolved in a few c.c. of water, and an excess of sodium phosphotungstate added. The precipitate, consisting of mucilage, albumose, and peptone, is weighed on a tared filter. It is then incinerated, and the weight of the ash, as also the weights of the mucilage and albumose, deducted from that of the whole precipitate, the difference being peptone. *Unchanged substances*, consisting of amido-bases, fatty acids, and amido-acids, are determined in the alcoholic extract. Taurine, dextrose, and glycogen are insoluble in alcohol, and are determined by the difference between the determined substances and 100. The water, mineral matters, and insoluble substance are determined according to Bruylants' method (*loc. cit.*). The author adds the following analyses:—

	Peptone from albumin of cleaned meat.	Peptone from egg-albumin.	Peptone prepared directly from meat.
Peptone	37·675	34·700	25·857
Albumose	31 300	53·350	15·964
Mucilage	—	—	9 826
Unchanged products	5·525	5·930	29 972
Mineral matters	8·285	1·025	19·386
Water	10·250	4·625	—
Insoluble	9·965	3·980	—

J. W. L.

Quantitative Estimation of Furfuraldehyde and of Pentaglucoses (Pentoses). By A. GÜNTHER and B. TOLLENS (*Ber.*, **23**, 1751—1752).—The method of estimating furfuraldehyde by precipitating with ammonia as hydrofurfuramide does not yield very trustworthy results, and the authors propose instead to estimate it by titration with phenylhydrazine, employing aniline acetate as indicator, which gives results accurate to 1—2 per cent. They have also improved the process of distilling pentaglucoses (pentoses) with hydrochloric acid, so that the quantity of furfuraldehyde obtained is constant, and by estimating the latter they are therefore enabled to determine the quantity of pentaglucoses (pentoses) present.

Pure arabinose and xylose yield about 50 per cent.; cherry gum, 15 per cent.; gum arabic, 14 per cent.; and wheat and oat straw, 13 per cent. by weight of furfuraldehyde. On the other hand, starch and sugar only yield $\frac{1}{4}$—$\frac{1}{3}$ per cent., and ivory-nut shavings, about 1 per cent. Glycuronic acid, however, yields about 46 per cent.

H. G. C.

General and Physical Chemistry.

Dispersion of Carbon Compounds. By P. Barbier and L. Roux (*Compt. rend.*, **111**, 180—183; compare Abstr., 1889, 865, this vol., p. 1034).—Measurements of the refractive and dispersive powers of simple and mixed ethers of the methane series show that the dispersive power and the specific dispersive power increase with the molecular weight, but are practically the same for all isomerides containing the same quantity of carbon. The introduction of CH_2 into the molecule raises the specific molecular dispersive power by about 8·2. In the equation $\left(\frac{B}{d} - b\right)M = a$, the value of a is $-6·443$, and of b $+0·5790$; in the equation $(B - \beta)\left(\frac{M}{d}\right)^{\frac{1}{3}} = K$, $\beta = 0·6626$ and $K = -1·44$.

In methyl allyl, ethyl allyl, and propyl allyl ethers, the dispersive power and specific dispersive power remain practically constant, and do not increase with the molecular weight. Comparing these ethers with others containing the same number of carbon atoms, it is seen that the dispersive power increases as the proportion of hydrogen diminishes.

In the case of methyl benzyl, ethyl benzyl, propyl benzyl, isobutyl benzyl, and amyl benzyl ethers, the dispersive power diminishes as the molecular weight increases, but the addition of CH_2 produces a variation in the specific molecular dispersion equal, as in the methane series, to about 8·2. For the series in the first equation, $a = +40·87$, and $b = +0·5834$; in the second equation, $\beta = 0$, and K about 4·4.

In all cases the specific molecular dispersive power of the ethers is equal to the sum of the dispersive powers of the two alcohols from which they have been formed, minus the dispersive power of the water eliminated. C. H. B.

Dispersive Power of Acids of the Acetic Series. By P. Barbier and L. Roux (*Compt. rend.*, **111**, 235—236).—The dispersive power of acids of the acetic series increases with their molecular weight. Formic acid is an exception, if the dispersive power B is alone considered, but the exception disappears in the case of the specific dispersive power. The dispersive powers of isomerides are practically the same, but the values are highest in the case of the normal acids. The differences between the successive values of the specific molecular dispersive powers are practically constant, and equal to 7·8, so that the variation of the specific dispersive power may be represented as a function of the molecular weight, thus, $\left(\frac{B}{d} - b\right)M = a$, in which $a = -11{,}515$, $b = 0·5625$. The relation between the dispersive power and the molecular volume is the same as in the case of the corresponding alcohols (this vol., p. 1034), the values of the constants being $\beta = +0·6393$, $K = -1·08$. C. H. B.

Dichromate Cell. By GENDRON (*Dingl. polyt. J.*, **275**, 68—70).—This cell, in which potassium or sodium dichromate forms the depolarising fluid, is capable of yielding a powerful current for a lengthened period. The area of its electrodes is large in proportion to the capacity of the cell; the internal resistance is small, the electrodes being placed parallel, and as closely to one another as is practicable. The zinc plates are readily exchanged without the necessity of interrupting the current, the fluid can be kept at a constant level, whilst the spent liquor is removed from the lower part of the cell by the aid of an automatic arrangement of valves, full details and drawings being given in the original. D. B.

Theory of Secondary Batteries. By F. STREINTZ and G. NEUMANN (*Ann. Phys. Chem.* [2], **41**, 97—112).—Streintz, in a former paper (this vol., p. 315), showed the electromotive behaviour of the plates of a secondary cell on charging and discharging. The authors now endeavour to fix the chemical reactions which take place at the same time, and for this purpose investigate the difference of potential exhibited by various lead compounds with respect to an amalgamated zinc plate. The compound was pressed into two strong glass vessels, one provided with a platinum, the other with a bright lead electrode. The zinc plate was immersed in dilute sulphuric acid, and connection made with the substance by means of a woollen thread moistened with the acid. The lead or platinum electrode was connected with one pair, the zinc plate with the other pair of quadrants in a sensitive electrometer. When the same result was obtained with lead as with platinum, it was concluded that the conduction was metallic; when otherwise, electrolytic. The lead compounds investigated were the oxides Pb_2O, PbO, Pb_3O_4, PbO_2; the hydroxides $Pb(OH)_2$, $PbO(OH)_2$; and the sulphate. The peroxide was the only substance that showed metallic conduction, and in general the difference of potential against zinc increased in the case of the oxides and hydroxides with the quantity of oxygen they contained.

The authors formulate their conclusions as follows:—The phenomena in a secondary cell are sufficiently explained by the behaviour of metallic lead, its sulphate, and its peroxide, together with the gaseous ions, oxygen and hydrogen. On discharging, the metallic surface of the negative plate is converted into sulphate, which passes in part into peroxide; whilst the peroxide of the positive plate is superficially converted into sulphate. On charging, the sulphate disappears from both plates, and finally the negative plate consists entirely of lead and absorbed hydrogen, the positive plate of pure peroxide. (Compare Frankland, this vol., p. 842.) J. W.

Electrical Properties of Semi-permeable Walls. By W. OSTWALD (*Zeit. physikal. Chem.*, **6**, 71—82).—A semi-permeable material is looked on as one which allows the passage through it of the solvent, but not of the dissolved salt. The permeability of any given material does not, however, depend on the nature of any given salt as a whole, but on that of each of its ions. Ferrocyanide of

copper is permeable by potassium chloride, because it allows the passage of both the potassium and chlorine ions, not by barium chloride, because it will not allow the passage of the barium, and not by potassium sulphate, because it will not allow the passage of the SO_4 ions.

If a solution the ions of which cannot pass through a semi-permeable material, be submitted to electrolysis, the electrodes being separated by a semi-permeable wall, the latter will itself act as a metallic electrode. Two glasses were filled with normal copper sulphate solution, and connected by a U-tube, the ends of which were covered with parchment paper. The U-tube was filled with normal potassium ferrocyanide, so that a layer of copper ferrocyanide formed on the paper, and a current was then passed from one glass to the other. After a time, copper was found deposited on the parchment paper in the glass which contained the positive electrode. The mechanism of the process appears to be that the positively-charged copper ions come in contact with the ferrocyanide film, through which they cannot pass, and therefore here give up their charges, and are deposited in the metallic state. The same thing happens to the negative $FeCy_6$ ions at the other side of the film. These, by loss of an equivalent of negative electricity, become converted into the triad ferricyanide ions. At the other film, the potassium ions, which can permeate the copper ferrocyanide, pass through and unite with the SO_4 ions of the copper sulphate, and so establish electrical equilibrium.

This view of the peculiar behaviour of semi-permeable materials towards different ions affords an explanation of the fact noticed by Becquerel that when a tube containing copper nitrate solution is placed in a solution of sodium sulphide, a deposition of copper takes place in the interior of the tube. In this case, the copper sulphide first formed allows the passage of the NO_3, but not of the copper ions. The NO_3 ions coming in contact with the sodium sulphide bring about the following change :—

$$\begin{array}{cccccccccc} 2NO_3 & + & 2Na_2 & S & = & 2Na & NO_3 & + & K_2 & S_2. \\ 2(-) & & 4(+) & 4(-) & & 2(+) & 2(-) & & 2(+) & 2(-). \end{array}$$

If the positive and negative charges are counted, it will be seen that there are six negative and four positive before, and four negative and four positive after the reaction. The negative charges set free combine with the positive charges of the copper ions on the other side of the film, and the metal is thus deposited.

The author shows that many electrophysiological phenomena are explained by the above facts with regard to semi-permeable materials, as that of the secondary resistance of albumin noticed by Dubois-Reymond (*Monatsber. Berl. Akad.*, 1860, 816). The fact that damp membranes may, under circumstances, act as perfect insulators is also thus explained. H. C.

Difference of Potential between two Dilute Solutions of Binary Electrolytes. By M. PLANCK (*Ann. Phys. Chem.* [2], **40**, 561—576).—In a former paper (this vol., p. 677), the author calcu-

lated the difference of potential for the case of two solutions containing the same electrolyte in different proportions. The integration of the differential equations for the general case of two solutions containing different electrolytes is the subject of this communication. The existence between the two solutions of a limiting layer of small but still finite thickness is assumed. Different values for the difference of potential are found according to the way in which the concentration is supposed to alter within the intermediate layer. The author shows, however, that in a very short time a state of stability will be reached in which the total concentration (sum of the concentrations of the positive or negative ions) will vary within the layer as a linear function of the distance. This consideration is sufficient to make the above problem uniquely soluble, supposing the electrolytes to be completely dissociated. A comparison of the calculated values for the difference of potential with Nernst's experimental numbers shows a satisfactory agreement. J. W.

Electrical Resistance of the Alloys of Ferro-manganese and Copper. By E. L. Nichols (*Amer. J. Sci.* [3], **39**, 471—477).—The resistance of alloys of ferro-manganese and copper was determined at 20° and 100°, the object being to investigate the change of resistance with change of temperature between these limits. In the course of these experiments, it was found that a number of the alloys had the remarkable property of decreasing in resistance each time that they were subjected to a change of temperature, an alloy containing 80·82 per cent. of copper and 19·12 per cent. of ferro-manganese, when heated and cooled through the above range of 80°, diminishing in resistance with each operation, the diminution being still perceptible at the end of the seventh cycle. On being then raised to a red heat and allowed to cool, a still more marked diminution in the resistance of the above alloy was found to have taken place. The temperature coefficient of this alloy was positive, and continued to increase as the heating and cooling process was repeated. With an alloy consisting of 70·65 parts of copper and 29·35 parts of ferro-manganese, a similar behaviour was observed. After being brought into a condition of stability such that further heating and cooling through a range of 80° had but little permanent effect upon its conductivity, it still showed, when hard drawn, an appreciable negative coefficient. It was then annealed three times at red heat, specific resistance and coefficient being determined for the range of 20° to 100° after each annealing. The results were as follows:—

Condition.	Specific resistance.			Coefficient.
	20°.	100°.	20°.	
Rather hard	46·10	45·99	46·09	−0·000024
Once annealed	45·10	45·18	45·09	+0·000021
Twice annealed	44·07	44·33	44·06	+0·000068
Thrice annealed	42·76	43·58	42·74	+0·000192

A number of similar alloys showed, when hard rolled, a coefficient very near to zero, sometimes positive, sometimes negative. After annealing at 300° to 400°, a well-defined negative coefficient, after annealing at a red heat, a still larger positive coefficient, was produced. It was found that the positive coefficient produced by annealing could be reduced again by rolling the alloy.

The relation of composition to the temperature coefficients was determined. With 10 per cent. of ferro-manganese, the change of resistance is less than 1 per cent. for 100°. Alloys containing from 15 to 20 per cent. of ferro-manganese have exceedingly small coefficients, the coefficient at 18 per cent. being practically zero. As above shown, the coefficient may be made to undergo a considerable alteration by varying the temper of the metal. The marked influence of temper upon the conductivity of these alloys renders it difficult to determine the precise law of the change in specific resistance with the composition. It would, however, appear from the results that the resistance increases nearly in direct proportion to the percentage of ferro-manganese. H. C.

Conductivity of Distilled Water. By W. OSTWALD (*Ann. Phys. Chem.* [2], **40**, 735—737).—The author contends, as against Pfeiffer, that the electrical conductivity of distilled water is in great measure due to the presence of carbonic anhydride in solution, which can only be removed by distillation over a considerable quantity of a base, by preference lime. J. W.

Behaviour of Mannitol towards Boric Acid. By G. MAGNANINI (*Zeit. physikal. Chem.*, **6**, 58—70).—It is well known that some action takes place between boric acid and mannitol when in solution, and the assumption has been made that the two combine to form ethereal salts. In order to test this view, the author has determined the conductivity of solutions of boric acid containing different amounts of mannitol. The apparatus used was that described by Ostwald (Abstr., 1889, 4), and the molecular conductivities μ'_v and μ''_v of boric acid and of mannitol were calculated on the assumption that in each case the conductivity was due solely to the presence of one of the two substances.

The molecular conductivity of boric acid is found to be enormously increased by the addition of mannitol, the increase being greater the larger the amount of mannitol added. One must therefore assume, since mannitol is a non-conductor, that some electrolyte is formed in the solutions, increasing in amount with the mannitol added. It further appears that the molecular conductivity of boric acid in the presence of mannitol decreases with rising dilution, a behaviour which is opposed to that of all other electrolytes. One may, however, assume in this case that the compound of boric acid and mannitol first formed is subject to hydrolysis, and therefore will be decomposed by the addition of water. The decomposition of the electrolyte with increasing dilution then explains the decrease in the conductivity which takes place. This view is further supported by the fact that solutions containing a large proportion of mannitol behave normally

up to a certain dilution, the conductivity regularly increasing; but a maximum is after a time reached, and a decrease then sets in, no doubt due to the fact that the hydrolytic has become greater than the electrolytic dissociation.

Application of the Guldberg-Waage theory leads to the conclusion that a compound of boric acid and mannitol is formed in the above solutions, containing 3 molecules of the former to 1 molecule of the latter. The amount formed at constant temperature is a function of the amounts of water, boric acid, and mannitol, and may be determined with respect to the last two substances in accordance with the laws of chemical equilibrium, since the electrical conductivity of a solution containing different amounts of boric acid and mannitol in the same amount of water varies in accordance with the same laws.

Other substances containing hydroxyl groups are found to increase the conductivity of boric acid solution. Dulcitol was examined, but a simple relation was not found in this case. Measurements are also given for solutions of tartaric and boric acids, which lead to the conclusion that these form at least one compound with one another.

H. C.

Effects of the Silent Discharge. By P. SCHUTZENBERGER (*Compt. rend.*, **111**, 14—18; compare this vol., 691, 692, and 961).—The apparatus employed consisted of a vertical discharge tube, with armatures of acidulated water. The lower end of the tube was drawn out and connected, by means of a semi-capillary copper tube, with a horizontal glass tube 1·3 m. in length and 10 mm. in diameter, containing 0·3 m. of pumice and phosphoric anhydride, 0·25 m. of pumice and sulphuric acid, 0·25 m. of moist potash-pumice, and 0·25 m. of spongy platinum. The spongy platinum was kept at a dull red heat, in order to remove the last traces of oxygen from the combustible gases used in the experiments.

A current of gas was passed slowly through the apparatus, and was subjected to the action of the discharge. Under these conditions, the gas in the annular space through which the discharge passed was continually renewed, and the gaseous products were carried forward into the collecting apparatus, which contained phosphoric anhydride to absorb the water, and potash to absorb the carbonic anhydride.

A slow current of carbonic oxide was passed through the apparatus for six hours without any discharge; there was no alteration in the weight of the collecting apparatus. Four experiments were made with the discharge, from 0·2 to 0·3 gram of solid matter being condensed in each case. In three experiments this product was deep brownish-black, and in one it was pale-brown in colour. It was only very partially soluble in water, and the brownish-yellow solutions were very feebly acid. The proportion of hydrogen did not exceed 0·2 to 0·3 per cent., and the ratio of carbon and oxygen was $C_4 : O_3$ in one case, and $C_5 : O_4$ in another.

A soluble and acid product obtained by renewing the gas in the apparatus at the end of every three hours only had the composition C, 42·1 ; H, 1·4 ; O, 56·5 per cent.; whilst when the water and carbonic acid were absorbed every half hour, the results were as follows :—

C per cent.	H per cent.	O per cent.
47·28	0·48	52·24
45·02	0·60	54·38
45·00	0·59	[illegible]·[illegible]1

The longer the action of the discharge on the same quantity of gas, the greater the proportion of hydrogen and oxygen in the condensed product. The solubility and acidity increase with the time of action, and the ratio between the carbonic anhydride formed and the condensed product diminishes up to a certain limit. In four experiments in which the gas was continually renewed, the ratio of the weight of the condensed product to the weight of the carbonic anhydride formed was 1·39, 1·38, 1·39, 1·35, whilst the continued action of the discharge on one and the same mass of gas gave a ratio of 2·2 after an hour, and 2·5 to 2 6 after four days. The ratio of the oxygen and hydrogen in the condensed product is not the same as in water; there is an excess of oxygen. From the composition of the condensed product and the weight of gaseous carbonic anhydride formed at the same time, it follows that only about half the oxygen required to produce the carbonic anhydride has been obtained from the condensed carbonic oxide, and hence oxygen must have been derived from external sources. Moreover, the oxygen introduced from without is more than could exist in combination with the hydrogen (also derived from external sources) in the form of water.

If a current of pure and dry nitrogen is passed through the apparatus, and is subjected to the action of the discharge, there is no alteration in the weight of the absorbing apparatus, and hence it follows that the elements of water do not pass through the glass in a combined condition, and, moreover, do not pass through cracks or pores in the glass. It would seem that the oxygen and hydrogen pass separately through the glass by a kind of electrolytic transportation, and are detected only when they come in contact in the annular spaco with some substance, such as acetylene, which can combine with the oxygen, or carbonic oxide, which combines with both oxygen and hydrogen. C. H. B.

Influence of a Magnetic Field on the Electrical Resistance of Gases. By A. WITZ (*Compt. rend.*, **111**, 264—266).—A magnetic field has no influence on the silent discharge in gases; its effect in the case of a Geissler tube must be attributed to the special construction of the tube, and the state of rarefaction of the gas which it contains. Such tubes seem to behave like condensers, and the effect of a magnet may be attributed to an alteration in their electrical capacity.

C. H. B.

Heats of Formation of Amides. By BERTHELOT and FOGH (*Compt. rend.*, **111**, 144—146).—The last column gives the heat of formation from the solid acid and the crystalline base with elimination of water.

	Molecular heat of combustion.		Heat of formation from elements.	Heat of dissolution at 14—14·5°.	
	Const. vol.	Const. press.			
Acetamide	283·0	288·1	72·9	−1·85	− 5·0
Propionamide..	435·6	436·0	88·4	−0·97	—
Benzamide	851·9	852·3	49·3	—	− 5·6
Succinimide ...	439·3	439·2	110·5	—	−23·1
Acetanilide....	1016·1	1016·8	52·1	—	+13·9
Benzanilide ...	1582·2	1583 7	22·1	—	+ 7·1

The formation of the anilides develops more heat than the formation of the corresponding amides, a result which explains their greater stability in contact with water, the difference being increased because the heats of formation of the ammonium salts are greater than those of the aniline salts. C. H. B.

Heats of Formation of Sugars. By Berthelot and Matignon (*Compt. rend.*, **111**, 11—14).—

	Mol. wt.	Heat of combustion, 1 gram.	Molecular heat of combustion.		Heat of formation.
			Const. vol.	Const. press.	
Erythrol	122	4117·6	502·3	502·6	+219·6
Arabinose........	150	3714·0	557·1	557·1	+259·4
Xylose...........	150	3739·9	560·7	560·7	+255·8
Raffinose	504	4020·0	2026 1	—	+775·3
Inosite (racemic)..	180	3676·8	661·8	—	+318·0
Inosite (inactive)..	180	—	666·5	—	+313·3

The heat of formation of dextrogyrate and of lævogyrate inosite is 316·2 Cal., from which it follows that the inactive inosite contains a reserve of energy.

Heat of dissolution of erythrol at 24°, −5·54 Cal. Heat of dissolution of anhydrous raffinose at 18·1°, +8·38 Cal.; of hydrated raffinose at 17·7°, −9·72 Cal.

Differences between Heats of Formation.

Methyl alcohol (liquid) and glycol (liquid)........	+113 Cal.
Glyercol (crystallised) and erythrol (crystallised)	+114 ,,
Erythrol (crystallised) and mannitol (crystallised)	+113 × 2 Cal.

Ethyl alcohol and glycol	+41·5 Cal.
Propyl alcohol and glycerol	+42·7 × 2 Cal.
Butyl alcohol and erythrol	+43·5 × 3 ,,

From the last three numbers it will be seen that the heat of substitution of hydroxyl, OH, for hydrogen, H, increases in proportion to the hydricity of the alcohol. They also represent the difference between the heat of fixation of CH_2 (about 156 Cal.) and CHOH (about 113 Cal.).

C. H. B.

Heats of Combustion of Sulphur Compounds. By BERTHELOT and MATIGNON (*Compt. rend.*, **111**, 9—11).—Determinations of the heats of combustion of carbon compounds containing sulphur have hitherto been somewhat unsatisfactory, owing to the difficulty of ensuring complete oxidation of the sulphur. If, however, the compound is burnt in a calorimetric bomb filled with oxygen under a pressure of 25 atmospheres, the oxidation of the sulphur is complete and instantaneous (compare this vol., p. 1462). If the compound contains very little hydrogen, the addition of camphor is necessary.

	Heat of combustion, 1 gram.	Molecular heat of combustion.		Heat of formation.
		Const. vol.	Const. press.	
Thiophen	7970·1	669·5	670·9	− 14·9
Taurine	3080·6	385·0	385·7	+ 185·7
Carbon bisulphide (liquid)	5217·0	396·4	398·1	− 22·6

Heat of formation of gaseous carbon bisulphide, −27·0 Cal.

C. H. B.

Stability of Salts alone and in presence of Water: Aniline Salts. By BERTHELOT (*Compt. rend.*, **111**, 135—144).—*Aniline Sulphate*:—Molecular heat of dissolution (284 grams) at 24°, −4·63 Cal.; heat of neutralisation of aniline by one equivalent of sulphuric acid, + 8·63 Cal. The heat of dissolution of aniline is given by the equation Q = −(t—11·9)0·0447 Cal., and hence the neutralisation of one molecule of dissolved aniline by an equivalent of dilute sulphuric acid develops +9·21 Cal., a number 5·3 Cal. lower than the corresponding value for ammonia. The difference between the heats of formation of the two solid salts from dissolved base and acid is 4·3 Cal., and from gaseous constituents 5·1 Cal. The addition of an equivalent of sulphuric acid to a molecule of aniline sulphate absorbs −0·81 Cal., or, as in the case of sodium, potassium, and ammonium, the heat of formation of the acid sulphate is lower than that of the normal salt. An excess of aniline produces no sensible thermal disturbance, a fact which shows that combination between the base and the acid is very nearly, if not quite, complete. Nevertheless, aniline sulphate in solution undergoes slight dissociation, especially when heated, the extent of dissociation, although small, being distinctly greater than in the case of ammonium sulphate.

Thermochemical measurements show that sodium hydroxide completely displaces aniline from its sulphate even in presence of an

excess of aniline. Ammonia also displaces the aniline, but in this case there is a slight division of the acid between the bases, a result due to the partial dissociation of the two sulphates in solution.

Aniline Nitrate and Chloride.—These salts stand in precisely the same relation to the corresponding ammonium salts as does aniline sulphate to ammonium sulphate. In the case of both bases, the heats of formation of the nitrate and chloride from the acid and base are the same.

Aniline acetate has not been isolated in the solid state. The addition of acetic acid to an equivalent quantity of aniline at 24° develops +1·53 Cal., and if it is assumed that the heat of fusion of the acetic acid is the same as that of aniline acetate, the heat of formation of this salt from gaseous constituents is +10·1 Cal. The heat of formation of the ammonium compound is + 8·4 Cal. greater, and hence the combination of aniline with acetic acid is much less complete than with the acids previously mentioned. A solution of aniline and acetic acid in equivalent proportions gives a further development of + 1·41 Cal. on addition of a second equivalent of acetic acid, and + 0·73 Cal. with a second equivalent of aniline. In solution, therefore:

$NH_2Ph + HOAc$	develops	+3·8 Cal.
$NH_2Ph + 2HOAc$ ..	,,	+5·2 ,,
$2NH_2Ph + HOAc$	,,	+4·8 ,,

Aniline Benzoate.—Aniline and benzoic acid, when gently heated together in equivalent proportions, yield a homogeneous liquid which crystallises on cooling and dissolves completely in water. If the solution is concentrated by evaporation, it deposits crystals of benzoic acid, and the dissociation of the salt is practically complete. The heat of dissolution of the crystalline product is −4·79 Cal., and from this and the heat developed by the action of sodium hydroxide it follows that the action of the liquid aniline on the solid acid develops + 2·7 Cal. The heat of formation of the benzoate from gaseous constituents would be + 11·3 Cal., and the difference, 5·7, between this number and the value for the ammonium salt is nearly the same as in the case of the nitrates. The formation of the solid salt from dissolved acid and base is + 9·8 Cal., or 5 Cal. higher than in the case of the acetate. It follows that though the salt partially dissociates on solution, the dissociation is much less than in the case of the acetate.

The crystalline product spoken of as aniline benzoate is really a mixture of crystals with an oily substance, and if the crystals are separated by repeated pressing between filter paper, they are found to have the composition of the acid benzoate, $PhNH_2,2C_7H_6O_2$.

C. H. B.

Equilibrium and Reciprocal Displacements between Volatile Organic Bases. By BERTHELOT (*Compt. rend.*, **111**, 289—296; compare preceding abstract).—*Piperidine* is alkaline to litmus, and when treated with water, heat is developed in gradually increasing quantity; $C_5H_{11}N + 1\frac{1}{6}H_2O$ develops +1·6 Cal.; + $3H_2O$, +2·3 Cal.; + $9H_2O$, +3·5 Cal.; + $300H_2O$, +6·46 Cal. These results indicate the formation

of a partially dissociated hydrate, and in this respect piperidine resembles trimethylamine. The tertiary bases, in fact, show in a well marked degree that power to combine with the elements of water which characterises the quaternary bases. This fact has to be taken into account in determinations of the heats of neutralisation of these compounds.

$C_5H_{11}N$ diss. + HCl diss. develops +13·32 Cal.; $C_5H_{11}N$ liq. + HCl gas = $C_5H_{12}NCl$ solid, develops +38·2 Cal.; $C_5H_{11}N$ gas + HCl gas = $C_5H_{12}NCl$ solid, develops +46 Cal. These numbers are of the same order of magnitude as the corresponding numbers for the ammonium compounds.

$C_5H_{11}N$ diss. + $\frac{1}{2}H_2SO_4$ diss. develops +15·5 Cal.; $C_5H_{11}N$ diss. + H_2SO_4 diss. develops +14·3 Cal. As in the case of pyridine and the alkali metals, the heat of formation of the normal salt is greater than that of the hydrogen salt.

Both piperidine and ammonium salts are slightly dissociated in solution, and there is reciprocal displacement to a certain extent when the salts are mixed. $C_5H_{11}N$ diss. + NH_4Cl diss., develops +0·4 Cal. and $C_5H_{11}NHCl$ diss. + NH_3 diss. absorbs −0·45 Cal., the sum of the two differences being practically identical with the difference between the heats of neutralisation.

The author is unable to confirm Colson's statement (this vol., p. 1368) that piperidine displaces calcium from calcium chloride. On the contrary, the thermal disturbances show that sodium hydroxide and calcium hydroxide displace piperidine almost, if not quite, completely, from solutions of its hydrochloride, and freshly precipitated calcium hydroxide readily dissolves in strictly equivalent proportions in a solution of piperidine hydrochloride. If the piperidine has been exposed to the air and has absorbed carbonic anhydride, then it precipitates calcium salts, and if carbonic anhydride is passed into a solution of calcium chloride containing piperidine, calcium carbonate is precipitated.

On the other hand, if piperidine is poured into a saturated solution of calcium chloride, a precipitate forms immediately, and the whole liquid becomes solid. The precipitate is not calcium hydroxide, but re-dissolves completely on addition of water. Calcium nitrate and acetate behave similarly, but the precipitate with the chloride requires the greatest quantity of water to dissolve it, and in this case also the development of heat is greatest. It is probable that these precipitates are compounds of the chloride or oxychloride with piperidine, analogous to the ammoniacal compounds of calcium and other metals. Piperidine also precipates barium chloride, but only from a saturated solution, and without decomposing it, the piperidine exerting a dehydrating action similar to that of hydrochloric acid. Like ammonia, however, piperidine precipitates magnesium salts.

Pyridine.—The data are as follows:—

C_5H_5N liquid + $220H_2O$ at 22°	develops	+2·12	Cal.
C_5H_5N diss. + HCl diss..................	,,	+5·1	,,
C_5H_5N diss. + $\frac{1}{2}H_2SO_4$ diss..............	,,	+7·1	,,
C_5H_5N liq. + $\frac{1}{2}H_2SO_4$ diss...............	,,	+9·22	,,
$C_5H_5N.\frac{1}{2}H_2SO_4$ + $\frac{1}{2}H_2SO_4$...............	absorbs	+0·87	,,

The first two values agree with Colson's determinations:—

C_5H_5N diss. + NH_4Cl diss.	develops	0·0 Cal.
C_5H_5N,HCl diss. + NH_3 diss....	"	+7·3 "

Ammonia displaces pyridine almost completely, but there is some evidence of a division of the acid, due to dissociation of the ammonium salt, as in the case of aniline.

The addition of pyridine to calcium chloride solution develops a small quantity of heat (0·12 Cal.), but there is no precipitate. If, however, carbonic anhydride is passed into the liquid, calcium carbonate is precipitated, a reaction which does not take place in the case of aniline.

In the case of piperidine and pyridine, there is some division of hydrochloric acid, but the greater part remains in combination with the first base.

Aniline.—The heats of formation of the salts of aniline are almost identical with those of the salts of pyridine, and when aniline is added to a solution of pyridine hydrochloride there is a partial displacement of the pyridine. Pyridine displaces aniline from its sulphate to a considerable extent, although not completely. In no case, in fact, is displacement by pyridine complete, the distribution of the acid being determined by the degree of dissociation of the two salts.

C. H. B.

Boiling Points of Substances are a Function of their Chemical Nature. By M. WILDERMANN (*Ber.*, 23, 1468—1470, and 2146—2151; compare this vol., p. 941).—The author quotes further instances in support of the law given in his previous paper with regard to the boiling points of substances. Objection is raised to the view recently put forward by Guldberg (this vol., p. 1043) that the ratio T/T_1, where T is the absolute boiling point and T_1 the absolute critical temperature, is practically constant; from which it also follows that the ratio T/T' of the two boiling points at the pressures n and np will be constant for substances the critical pressures of which do not greatly differ. It was shown by the author in the paper above quoted, that the relation of boiling point to pressure is a function of the chemical nature of a substance. The above ratio T/T' cannot therefore be the same function of the pressure for substances of different chemical nature, so that even if such substances have equal critical pressures, the values for the ratio T/T' will not be equal.

H. C.

Determination of the Vapour Pressures of Solutions. By G. CHARPY (*Compt. rend.*, 111, 102—103).—The solution is placed in a large test tube, the upper part of which contains a small condensation hygrometer. The space above the liquid is allowed to become saturated with the vapour of the solvent, the process being accelerated, if necessary, by reducing the pressure, and the dew point is determined. If the law of the variation of the vapour pressure of the solvent is known, the vapour pressure of the solution at the temperature of the experiment can be readily calculated. The accuracy of the determination is greater, the feebler the pressure that has to be

measured. This method is applicable to the case of solutions which attack mercury, and which, therefore, could not be introduced into a barometric tube. C. H. B.

Some Vapour-density Determinations. By A. KRAUSE and V. MEYER (*Zeit. physikal. Chem.*, 6, 5—9).—The method described by Demuth and Meyer (this vol., p. 440) for determining the vapour density of a substance below its boiling point is found to be still applicable when other gases such as air, nitrogen, or even carbonic anhydride are used in place of hydrogen to fill the vaporising bulb of the apparatus. The vaporisation is then much slower, but determinations of the vapour densities of xylene at 40°, and of paranitrotoluene at 33°, below their boiling points, in air and in carbonic anhydride, show that perfectly accurate results are obtained. The above gases may therefore be employed in cases where hydrogen cannot be used, but it is preferable to use the latter in all cases where possible.

Using the Dumas method, Cahours found that the theoretical vapour density of acetic acid is first reached at 250°. The authors find that by their method the theoretical vapour density can be reached at about 160°. The results obtained were as follows:—

Temp.	Krause and Meyer.		Cahours.	Temp.	Krause and Meyer.		Cahours.
100°	2·67	2·60	—	160°	2·12	2·18	2·48
125	2·51	2·42	3·20	190	2·14	2·07	2·30
140	2·28	2·26	2·90	—	—	—	—

The theoretical number is 2·08.

Iodine, according to Troost, at the temperature of boiling sulphur, already shows dissociation when under a reduced pressure. No sign of dissociation was, however, found by the authors when iodine was allowed to vaporise at the above temperature in the presence of a large excess of air. An experiment performed with sulphur at the same temperature, and in an atmosphere of nitrogen, gave a vapour density corresponding with S_7. This is looked upon as accidental, as the vapour density is not constant at these temperatures. H. C.

Osmotic Experiment. By W. NERNST (*Zeit. physikal. Chem.*, 6, 37—40).—If we have two solutions in the same solvent of different concentrations, separated by a layer of a second liquid in which the solvent is soluble, but not the dissolved substance, the liquid will act as a semi-permeable material, allowing the passage of the solvent from the solution of less to that of greater concentration, but not allowing the passage of the dissolved substance. This is shown to be the case with solutions of benzene in ether separated from one another by a membrane saturated with water. H. C.

Rôle of Solid Substances in Chemical Equilibrium. By A. HORSTMANN (*Zeit. physikal. Chem.*, 6, 1—4).—It is a matter of

common experience that the relative amount of a solid substance exercises no influence on chemical equilibrium, or, as it is usually expressed, the active mass of a solid substance appears to be constant. Thus when carbonic anhydride is in contact with a mixture of calcium carbonate and lime, although seemingly the mixture should absorb a greater quantity of carbonic anhydride, the greater the amount of lime present, this is not found to be the case, the tension of the gas being independent of the proportion of the two solids in the mixture. This fact has not hitherto been satisfactorily explained, but Van't Hoff's recent views with regard to the existence of solid solutions (this vol., p. 1044) now open out a way for such an explanation.

Two solid substances, A and B, will, as a rule, form with one another two saturated solutions, the one containing a small quantity of B in a large quantity of A, and the other a small quantity of A in a large quantity of B. Under these circumstances, equilibrium will, within very wide limits, be independent of the proportion of the two solids. In the case of calcium carbonate just considered, one may assume that there are two solutions, one containing aCaO in $100CaCO_3$, and the other $b CaCO_3$ in 100CaO, where a and b are both small quantities. According to a well known thermodynamic principle, the tension of carbonic anhydride above these two solutions must be the same, and this will remain constant as long as the two solid solutions are present at the same time, whatever be the relative amounts of the solid substances; for the addition or removal of carbouic anhydride can only alter the amounts of the two solutions, but not their composition, and hence the tension also remains unaltered. The tension will only become variable when the quantity of one of the constituents is so small that only one of the two solutions can be formed. H. C.

Affinity Coefficients of Alkyl Halogen Compounds and of Amines. By N. MENSCHUTKIN (*Zeit. physikal. Chem.*, 6, 41—57).—In a former paper (Abstr., 1888, 901), the author has shown that the nature of the solvent exercises a very material influence on the velocity of the chemical reaction there studied. In order to submit this influence to a further examination, the velocity of the action of triethylamine on ethyl iodide in various neutral and chemically indifferent solvents was determined. The following table gives the comparative values of the velocities in different solvents, that in benzyl alcohol being taken as 100 (the greatest velocity):—

	Hydrocarbons.		
Hexane	0·13	Xylene	2·2
Heptane	0·17	Benzene	4·4
	Halogen Compounds.		
Propyl chloride	4·0	Bromobenzene	20·3
Chlorobenzene	17·4	α-Bromonaphthalene	84·9
	Ethers.		
Ethyl isoamyl ether	0·47	Phenetoïl	16·0
Ethyl ether	0·57	Anisoïl	30·3

Ethereal Salts.

Isobutyl acetate	4·3	Ethyl benzoate	19·4
Ethyl acetate	16·7		

Alcohols.

Isobutyl alcohol	19·4	Allyl alcohol	32·5
Ethyl alcohol	27·5	Methyl alcohol	38·0

Ketones.

Acetone	45·7	Acetophenone	97·3
Acetone (14·5 vol). Water (0·5 vol.)	66·9		

The velocity is least for the hydrocarbons and ethers; then come the ethereal salts and alcohols, and lastly the ketones, for which the velocity is greatest. Comparing members of the same homologous series, it is evident that the velocity is most retarded by compounds of highest molecular weight. Unsaturated compounds appear to assist the reaction, and this is especially noteworthy in the case of aromatic compounds. The velocities for the haloïd compounds are greater than those for the hydrocarbons, and bromine gives higher values than chlorine.

The velocity of the action of propyl iodide on triethylamine in different solvents was also studied. The numbers obtained are smaller than those for ethyl iodide, but a very similar relation is observed among them. The peculiar influence of the solvents in these cases justifies the conclusion that solutions in organic solvents are not mere mixtures, but that a distinct specific attraction exists between the solvent and dissolved substance. H. C.

Distribution of Hydrogen Sulphide between the Metals of two Dissolved Salts. By G. Chesneau (*Compt. rend.*, **111**, 269—271).—Hydrogen sulphide was added to a solution containing lead nitrate and copper nitrate in equal molecular proportions. Direct experiments showed that in the case of both salts incomplete or exact precipitation yields always a monosulphide. The division of the hydrogen sulphide between the two metals takes place in the direction indicated by the thermochemical data. Copper is precipitated more rapidly than lead, and the composition of the precipitate varies continuously with the proportion of hydrogen sulphide. The ratio of copper to lead also varies with the time during which the three compounds remain in contact; it first decreases, attains a minimum after a few minutes, and then gradually increases. C. H. B.

Berthollet's Laws. By A. Colson (*Compt. rend.*, **111**, 103—106). —Pyridine, aniline, and nicotine give no precipitate with solutions of calcium salts, and hence are exceptions to one of the laws of Berthollet. The heat of neutralisation of diisobutylamine is practically the same as that of calcium hydroxide, and, like the latter, the amine precipitates magnesium hydroxide, but is expelled from its salts by potassium hydroxide. Now if double decomposition depends

on affinity, and not on the nature of the base, the salts of diisobutylamine should not be decomposed by pyridine, aniline, or nicotine, and the author found that the sulphate and chloride are not decomposed, after first proving that the solubility of the amine in water is not affected by the presence of the other bases mentioned.

Organic and inorganic bases may be divided into two groups, the one being comparable to the alkalis, and the other to feebler metallic bases, the ratio established for one acid holding good as a general rule for all the others. When an alkaline base and a feeble base are simultaneously in presence of the same acid, the affinity of the alkaline base alone seems to be active, and the salts of the strong base are not decomposed by the feeble base, whatever be the nature and solubility of the bases, provided that they form soluble salts. In other words, Berthollet's laws do not hold good. From a thermochemical point of view, this fact may be stated approximately in the following terms: When two bases, by their separate union with the same acid, develop *very different* quantities of heat, the salts formed with the greater development of heat are not decomposed by the feebler base, whatever may be the direction of the interaction indicated by Berthollet's laws. C. H. B.

Reactions of Organic Bases. By A. Colson (*Compt. rend.*, **111**, 266—268).—Piperidine precipitates calcium from solutions of its soluble salts, although the heat of formation of piperidine chloride, +13 Cal., is less than that of calcium chloride, +14 Cal. Moreover, the heat of formation of piperidine chloride in any state is less than that of ammonium chloride, and yet ammonia does not precipitate solutions of calcium chloride.

Pyridine displaces aniline from solutions of its chloride, although the heat of formation of aniline chloride is greater than that of pyridine chloride. The result cannot be attributed to the formation of a pyridine dihydrochloride, for the latter is unstable in presence of water, and its beat of formation is very small.

It would seem that in these cases Berthollet's laws hold good, but the ordinary thermochemical laws do not, and the author concludes that for bases of the same order, Berthollet's laws are true, whatever the direction of change indicated by the thermochemical data.

C. H. B.

New Principle of Determining Molecular Weights. By W. Nernst (*Zeit. physikal. Chem.*, **6**, 16—36).—It has been shown by Van't Hoff and Tammann that iso-osmotic solutions have equal vapour tensions. Regarding the process of dissolution as equivalent to that of vaporisation (Nernst, this vol., p. 3), the tensions of different solutions towards any particular solvent will be subject to the same law. Hence if two iso-osmotic aqueous solutions are shaken, say, with carbon bisulphide, the latter will remove equal quantities of water from each. If the osmotic pressures of the solutions differ, that of lower osmotic pressure will part with more water than that with the higher. But since the osmotic pressure of a solution changes with the amount and the nature of the dissolved salt which it contains, the amount of water or other solvent which passes from the solution into

the carbon bisulphide or other liquid will vary as the dissolved salt varies. The osmotic pressure being also dependent on the molecular weight of the dissolved substance, there will obviously be a relation between this latter and the amount of solvent which will be dissolved out of the solution by some second liquid. This relation can be determined from thermodynamical considerations, and may be formulated as follows: The relative decrease in solubility towards some second liquid which a solvent undergoes, owing to the addition of some foreign substance, is as the number of molecules of the dissolved foreign substance to the number of molecules of the solvent. Hence if n is the number of foreign molecules dissolved in 100 mols. of the solvent, and a and a' the solubilities of the pure solvent and of the solution, $(a - a')/a' = n/100$. This law was tested and found to be correct for solutions of various substances in valeric acid and ether, the second liquid used in each case being water. The amount of valeric acid dissolved out by the water was determined in each case by titration, and the amount of ether by taking the specific gravities of the aqueous solutions. If x is the number of grams of a substance of molecular weight M dissolved in 100 gram mols. of the solvent, $n = M/x$, and we thus have a method of determining the molecular weight of the dissolved substance by measuring the solubility of its solution in some second solvent.

If a mixture of two liquids, such as ether and water, is cooled to a sufficiently low temperature, one of them, in this case the water, will begin to freeze. The point at which this will take place will be that corresponding to the reduction in the freezing point of water caused by the addition of the ether. If in the ether a third substance is dissolved which is not soluble in water, then, in accordance with the law stated above, the solubility of the ether in the water will be lessened, and hence the freezing point of the aqueous solution will rise If t_0 is the freezing point of a solution of pure ether in water, and t the freezing point after the addition of a foreign substance of molecular weight M, m grams of the latter being dissolved in 100 grams of ether, then $t/(t_0 - t) = 74m/100M$. The method can, therefore, be used to determine an unknown molecular weight, and experiments are quoted which demonstrate its correctness. Solutions other than those of ether and water may, of course, be used, if they fulfil the above necessary conditions. H. C.

Inorganic Chemistry.

Carbon an Impurity in Hydrogen affecting Determinations of its Atomic Weight. By E. W. MORLEY (*Amer. Chem. J.*, 12, 460—463).—All commercial varieties of zinc, including the purest zinc obtainable from the manufacturers of pure chemicals, when dissolved in dilute acids, give hydrogen containing carbon compounds, which are converted into carbonic anhydride on passing the gas over hot copper oxide. The hydrogen obtained by the electrolysis of an

alkaline hydroxide is likewise contaminated, unless care is taken to remove the carbonate present by precipitation with barium hydroxide. The bearing of these facts on the determination of the atomic weight of hydrogen is obvious, since hydrogen containing carbon compounds will have too high a specific gravity; and when weighed and burned, and the resulting water weighed, the atomic weight of hydrogen will appear to be too large.

The only known satisfactory method of obtaining pure hydrogen for atomic weight determinations is by the electrolysis of dilute sulphuric acid. The author, by this method, has succeeded in obtaining hydrogen, at the rate of from 10 to 20 litres per hour, in which there is no carbon, no sulphur; in which there is presumably no oxygen, and, finally, in which the resulting nitrogen is too small to be detected by a process which shows the presence of one-hundredth of a c.c. of nitrogen in a litre of hydrogen. G. T. M.

Atomic Weight of Oxygen. By W. A. Noyes (*Amer. Chem. J.*, **12**, 441—460; compare Abstr., 1888, 411, 647, and 649).—In a previous paper (Abstr., 1889, 672), the author expressed the opinion that some undiscovered source of constant error existed both in his and in Cooke's determinations of the atomic weight of oxygen. Further experiments, however, now show that such cannot be the case, and that the atomic weight lies very close to, and is probably very slightly less than, the value 15·896 (mean of 24 determinations). The apparatus used was the same in principle as that employed in his previous experiments (*loc. cit.*); the hydrogen was obtained by the electrolysis of a solution containing 15—20 per cent. of sulphuric acid. and every precaution was taken to remove impurities from it, and to prevent leakage in the apparatus. The author has shown that these two objects were attained.

Experiments made with the desire of substituting lead chromate, manganese dioxide, or litharge for the copper oxide gave unsatisfactory results; although, in the case of manganese dioxide, one determination, after necessary corrections for retained water had been allowed, gave the value 15·904. This result may be regarded as confirmatory of those obtained when the author employed copper oxide. G. T. M.

Density of Nitrogen and Oxygen according to Regnault, and the Composition of the Air according to Dumas and Boussingault. By A. Leduc (*Compt. rend.*, **111**, 262—264).—If the composition of the air by weight is calculated from the known composition by volume and the densities of oxygen and nitrogen as given by Regnault, the numbers obtained are, oxygen 23·58, nitrogen 76·42. According to Dumas and Boussingault the numbers are, oxygen 23·0 (22·9—23·1) and nitrogen 77·0. The author considers that this difference is most probably due to small errors in Regnault's numbers, namely, 1·10563 for oxygen and 0·97137 for nitrogen. Dumas found oxygen = 1·1057 and nitrogen = 0·972. Some preliminary determinations of the density of nitrogen by the author gave values between 0·972 and 0·973. C. H. B.

Rhombic Sulphur from Hydrogen Sulphide. By F. B. AHRENS (*Ber.*, **23**, 2708).—When pyridine or picoline is saturated with hydrogen sulphide and allowed to remain in open or loosely closed vessels, sulphur gradually separates out in small, lustrous crystals, consisting of rhombic octahedra. Those from picoline are larger, but less sharply developed than those from pyridine. It is probable that hydrogen sulphide first unites with the base forming an unstable additive compound, which is gradually decomposed by the oxygen of the air with separation of sulphur; the latter first remains dissolved in the base, but soon separates out in the crystalline form. This view is confirmed by the fact that the pyridine bases always contain water after the sulphur has separated H. G. C.

Action of Sulphurous Anhydride on Metals. By J. UHL (*Ber.*, **23**, 2151—2154).—Pure palladium foil decomposes pure dry sulphurous anhydride at a moderately high temperature in accordance with the equation—$Pd + 3SO_2 = PdS + 2SO_3$. The action ceases, however, after a short time owing, probably, to the fact that the metal becomes coated with sulphide. Platinum behaves like palladium under the same conditions, but gold decomposes the gas into sulphuric anhydride and sulphur.

When copper is heated in a stream of sulphurous anhydride, it is converted into cuprous sulphate and cuprous sulphide, a small quantity of a colourless sublimate being also formed; if the product is treated with water to dissolve the sulphate, and the dried residue containing copper sulphide is heated in a stream of hydrogen, evolution of hydrogen sulphide takes place. It was also found that freshly prepared, well dried copper sulphide is decomposed by hydrogen at a dull red heat with evolution of hydrogen sulphide; after about 15 minutes, the presence of metallic copper can be observed, and, on further heating, a considerable quantity of the sulphide is reduced. This fact proves that the method at present employed for the estimation of copper, namely ignition of the sulphide in a stream of hydrogen, cannot yield accurate results.

When silver is heated in a stream of sulphurous anhydride, it is converted into sulphate and sulphide, a very small quantity of sulphuric anhydride being also formed. Cadmium, under the same conditions, is converted into the sulphate and sulphide; the sulphide is not decomposed on ignition in a stream of hydrogen.

Mercury and bismuth are not acted on by sulphurous anhydride at a moderately high temperature, but magnesium glows vividly in the gas, even when only gently heated, yielding the sulphate, sulphite, and sulphide. Antimony is converted into the orange trisulphide and trioxide on ignition in sulphurous anhydride; aluminium, zinc, nickel, and cobalt seem to be partially converted into the sulphides.

F. S. K.

Expansion of Silica. By H. LE CHATELIER (*Compt. rend.*, **111**, 123—126).—The following results were obtained with (1) a brick of tridymite obtained by treating a brick of quartz at 1600°, (2) chalcedony heated at 1500°; sp. gr. 2·16, (3) calcined quartz. The numbers represent the elongation in mm. per 100 mm.:

	15°.	95°.	130°.	170°.	245°.	270°.	360°.	480°.	570°.	590°.
(1.)	0·0	0·16	0·22	0·42	0·62	—	—	0·95	—	1·02
(2.)	0·0	0·06	—	0·20	1·23	—	1·29	—	—	—
(3.)	0·0	—	—	—	—	0·20	—	—	0·35	—

	600°.	650°.	700°.	900°.	990°.	1050°.
(1.)	—	—	1·09	1·07	—	1·05
(2.)	—	1·40	—	—	—	1·53
(3.)	0·41	—	—	—	0·45	—

Between 130° and 170°, the tridymite suddenly expands, the elongation being about 0·15 per cent., and this seems to correspond with the point of transformation, 130°, observed by Mallard. Tridymite shows a maximum expansion at about 750°, a phenomenon which has not previously been observed for any other substance. Between 170° and 245°, calcined chalcedony also shows a sudden elongation of 1 per cent., the exact temperature at which this takes place being 210°. It would follow from this transformation that this variety of silica cannot be regarded as amorphous. Calcined quartz expands continuously as the temperature rises, but the value of the elongation at 1000° is much lower than for any other variety of silica, and is intermediate between that of porcelain and that of glass; it follows therefore that when heated to a high temperature in presence of a small quantity of bases and suddenly cooled, quartz is really converted into amorphous silica. C. H. B.

Reduction of Oxygen Compounds by Magnesium. By C. WINKLER (*Ber.*, **23**, 2642—2668; see also this vol., pp. 331, 451, 693).—When a spiral of magnesium ribbon is ignited and plunged into carbonic anhydride, it continues to burn brightly, although in a somewhat altered manner, a slight, crackling noise being heard, whilst the burning particles of magnesium are projected against the sides of the vessel. The magnesia is coloured more or less grey from the presence of a little carbon, which is, however, only formed in very small quantity, carbon monoxide being the chief product. It is probable that the heat evolved by the burning magnesium dissociates the carbonic anhydride into carbon monoxide and oxygen, the latter then uniting with the magnesium vapour with explosive violence, and causing the above-mentioned scattering of the burning particles.

If a compact mass of magnesium ribbon be gently heated in a glass tube, and carbonic anhydride passed over it, the surface becomes rough, and covered with a greyish-black mixture of carbon and magnesium carbide, and carbon monoxide is found in the gas. At a full red heat, the magnesium ribbon bursts into flame, burning with an intense light, and forming a mixture of magnesia and charcoal. Magnesium wire under the same conditions does not ignite, but becomes coated with magnesium carbide; magnesium powder, on the other hand, causes formation of carbon monoxide below a red heat, and complete decomposition at a low red heat.

That magnesium can also cause the reduction of alkaline carb-

onates has been shown by Phipson (*Chem. News*, **9**, 219), and by the author (this vol., p. 331). In the instances already investigated, the metal formed is volatile, and it was, therefore, interesting to see whether the carbonates of the alkaline earths exhibit a similar behaviour. It was found that when 1 mol. of calcium carbonate was heated with 3 atoms of magnesium in powder, complete reduction took place at a red heat, with incandescence. The product on treatment with hot water and acids gave off hydrogen contaminated with other unpleasant smelling gases. If only 2 atoms of magnesium are employed, the products are quicklime, charcoal, and magnesia, whilst 1 atom of magnesium gives quicklime, carbon monoxide, and magnesia. The carbonates of strontium and barium behave in a similar manner, except that the reaction is much more violent. An attempt was made to obtain the carbon formed in the last reaction in a crystalline condition by fusing the product with an excess of aluminium. The dark-coloured metallic mass, however, on treatment with acids, left a black residue consisting of amorphous carbon and small crystals of barium aluminate.

Burning magnesium ribbon or wire is at once extinguished when plunged into carbon monoxide. If the gas be passed over the same form of magnesium at a red heat, it only becomes coated with magnesium carbide. The powder, however, burns at a red heat with a dull glow, forming a black, friable product, consisting apparently of a mixture of magnesia and charcoal. On treatment with acids, this leaves a sooty powder, which, however, in this, as in all the above cases, contains considerable quantities of magnesium. That the latter is chemically combined is shown by the fact that it is not attacked by concentrated hydrochloric acid. On ignition, it is slowly converted into magnesia, and quantitative measurements of the amount of the latter led to the impossible formula MgC_{10}. It is, therefore, probably a mixture of magnesium carbide and charcoal, and, moreover always contains impurities derived from the vessel in which the reduction is carried out. Attempts were made to obtain a definite compound Mg_2C by heating the two substances in the required proportions in a current of hydrogen, and by heating 1 mol. of calcium carbonate with 5 atoms of magnesium. In both cases, however, only a partial reaction takes place; the product undoubtedly contains magnesium carbide, and gives off unpleasant smelling gases on treatment with acids.

The researches of Wöhler (*Annalen*, **107**. 137, 369), Genther (*J. pr. Chem.*, **95**, 424), Phipson (*Proc. Roy. Soc.*, **13**, 217), and Parkinson (this Journ., 1867, 128) have shown the strong tendency of silicon to unite with magnesium, and it was, therefore, thought advisable to investigate the compounds thus formed before examining the action of magnesium on silica. Wöhler obtained a componnd to which he gave the formula Mg_4Si_3, whilst Geuther obtained a similar compound of the composition Mg_6Si_3. The author heated together magnesium and silicon in a current of hydrogen in the proportions required by the latter formula, and also in the proportion required by the formula Mg_2Si. Both products were very similar, the former having a slightly reddish tinge, whilst the latter is coloured pure greyish-

blue. Both readily lose magnesium on ignition, and the author believes that the true compound is Mg_2Si, and that the other compounds obtained are formed from it by loss of magnesium. Both compounds evolve spontaneously inflammable hydrogen silicide with hydrochloric acid of sp. gr. 1·190, but if dilute acid be employed, the gas is not as a rule spontaneously inflammable. A portion of the silicon passes at the same time into Geuther's hydrated silicon oxide, $Si_3H_2O_5$, and possibly also into silicoformic anhydride, $Si_2H_2O_3$, and silicone, $Si_4H_4O_3$. Dilute sulphuric acid behaves in a manner similar to dilute hydrochloric acid, but the concentrated acid is reduced to sulphurous acid and sulphur. With hydrofluoric acid, it yields hydrogen only, and is not completely dissolved, as it becomes coated with insoluble magnesium fluoride. It is not attacked by aqueous potash, but is readily decomposed by a solution of ammonium chloride, according to the equation: $2Mg_2Si + 8NH_4Cl + 3H_2O = 4MgCl_2 + Si_2H_2O_3 + 8NH_3 + 6H_2$. Magnesium silicide also decomposes the salts of many heavy metals, with precipitation of the metal, and even with neutral solutions of alkaline chlorides it yields hydrogen on boiling, the solution becoming alkaline. The formation of hydrogen must be secondary, and due to the previous formation of the alkali metal.

The action of magnesium powder on silica has been recently investigated by Gattermann (Abstr., 1889, 342). The author in his experiments employed very finely ground quartz. When mixed with 2 atoms of magnesium powder, the reaction is extremely violent, even when only small quantities are employed, and the product is never homogeneous, showing in some places the blue magnesium silicide, and in others the brown silicon. If to the mixture an equal weight of magnesia be added before heating, the reaction proceeds quite quietly. The product obtained without magnesia, when powdered and again heated in hydrogen, assumes a pure brown colour, and scarcely evolves any hydrogen silicide with hydrochloric acid, whence it appears that not only magnesium, but also magnesium silicide, can reduce silica to silicon. If, therefore, 1 mol. of silica be heated with 1 atom of magnesium, silicon alone is formed, the reaction proceeding much more quietly. From this it would also appear probable that a silicon monoxide SiO does not exist. Powdered silicates are also reduced at a red heat by magnesium powder in the same manner as silica itself.

When titanium dioxide (1 mol.) is heated with magnesium powder (2 atoms) at a red heat in a current of hydrogen, reduction takes place with incandescence. The product must be allowed to cool in an atmosphere of hydrogen, as otherwise it readily catches fire in the air. After remaining for a night under glacial acetic acid, it is partially dried at a moderate heat, and then completely in a current of hydrogen at 150°. A brown powder is thus obtained, which contains no metallic titanium, but a lower oxide of the metal, mixed with magnesium in the form of magnesium titanate. From the quantity of oxygen taken up on heating the reduction product, it appears probable that the reaction takes place according to the equation $2TiO_2 + Mg = TiO + MgTiO_3$. If, however, the quantity of mag-

nesium be decreased, products are obtained having the colours of the other lower oxides of titanium.

All attempts to prepare a compound of magnesium and titanium have been without success. A compound of titanium, hydrogen, and oxygen has, however, been obtained in the following manner. Titanium dioxide (1 mol.) was heated with magnesium powder (4 atoms) in a current of hydrogen. After cooling in the hydrogen atmosphere, the product was covered with water in a flask, and hydrochloric acid passed in drop by drop, until present in excess, almost pure hydrogen being evolved. The compound in suspension is collected, washed with hydrochloric acid, alcohol, and ether, and dried over sulphuric acid in a vacuum. It forms a black powder, which is not attacked by acids, and evolves hydrogen on treatment with aqueous potash, but remains unchanged in appearance. When heated by itself, it also gives off hydrogen without change of appearance, and on ignition in air forms titanic anhydride; the compound, however, still contains magnesium, probably as magnesium titanate. If in the numbers obtained on analysis the correction be made for a quantity of the latter compound corresponding with the magnesium found, the composition of the remainder is found to be Ti_3HO_4. The decomposition by heat would then be represented by the equation $Ti_3HO_4 = Ti_3O_4 + H$.

By the action of magnesium (2 atoms) on zirconium dioxide (1 mol.) at a red heat in a current of hydrogen, a black product was obtained which readily takes fire in the air, and which, after separating from unaltered magnesium, appears to have the composition ZrO, complete reduction to the metal not taking place. Zirconium monoxide may also be obtained by heating zirconium dioxide (1 mol.) and magnesium (1 atom). It is a deep-black powder, which readily undergoes oxidation forming titanium dioxide.

When zirconium dioxide and magnesium are heated in the proportion of 1 mol. of the former to 4 atoms of the latter, and the product treated just as described above under titanium, a black compound is obtained, which, like the titanium compound, is unacted on by acids, but evolves hydrogen on treatment with aqueous potash. On heating it, the flame of burning hydrogen is first seen, and then incandescence takes place, the dioxide being formed. From the analysis, it appears that, on the assumption that the magnesium found is present as zirconate, the new compound has the formula $Zr_3H_3O_4$. On heating by itself, it also evolves hydrogen, the reaction being possibly as follows:—$Zr_3H_3O_4 = 3ZrO + H_2O + H$.

The hydrogen evolved when the reduction product is treated with hydrochloric acid contains a small quantity of an impurity, which, from its general behaviour and peculiar odour, is probably hydrogen zirconide. H. G. C.

Beryllium. By G. Krüss and H. Moraht (*Ber.*, **23**, 2552—2556).—The authors have redetermined the atomic weight of beryllium. Beryllium oxide, purified as previously described (this vol., p. 697), was converted into the sulphate, $BeSO_4 + 4H_2O$, and weighed

quantities of this salt, most carefully purified by recrystallisation, were reconverted into the oxide by ignition. The average of 14 determinations gave 4·514 as the equivalent, or 9·028 as the atomic weight of beryllium (O = 15·96); when O = 16, the atomic weight is 9·05, an even smaller value than that found by Awdejew. These results show that the impurity to which the yellowish-green colour of concentrated acid solutions of beryllium chloride is due (*loc. cit.*) has caused the results of previous atomic weight determinations to come out too high; the nature of this impurity is being investigated.

F. S. K.

Action of Metallic Cadmium on the Halogen Cadmium Salts: Cadmium Sub-hydroxide and Sub-oxide. By H. N. MORSE and H. C. JONES (*Amer. Chem. J.*, **12**, 488—493).—When anhydrous cadmium chloride, contained in a long-necked flask of hard glass, is heated to the fusing point in a vacuum or in an atmosphere of nitrogen with an excess of metallic cadmium, the molten salt quickly assumes a fine garnet-red colour, which is not intensified by further heating. On cooling, the solidified mass has a greyish-white colour and a cleavage resembling that of talc or brucite; under the microscope, it appears homogeneous and free from metal; on analysis, it gives numbers which very closely approximate to those required by the formula Cd_4Cl_7. The new substance is a powerful reducing agent, and on heating fuses to a red liquid, which breaks up into metal and cadmium chloride; it is, perhaps, not a definite chemical compound, but a solution of cadmous chloride in cadmic chloride; and this view is supported by its behaviour towards water.

Anhydrous cadmium bromide, on similar treatment, behaves like the chloride, and gives a substance of the formula Cd_4Br_7; cadmium iodide appears to give a compound $Cd_{12}I_{23}$ (= $CdI + 11CdI_2$). The properties of both these substances closely resemble those of the above described chloride, and all three compounds, when treated with water, yield the ordinary halogen salts of cadmium which dissolve; a small quantity of hydroxide, which renders the water turbid; and heavy, transparent, highly-lustrous, crystalline substances, which rapidly lose their crystalline appearance, and change to a white, amorphous powder, which is cadmous hydroxide.

Cadmous hydroxide, CdOH, is a strong reducing agent. It dissolves in dilute acids, yielding with nitric acid, oxides of nitrogen; with other acids, free hydrogen. When gently heated, it loses water, and forms a heavy, yellow powder, which, under the microscope, is found to consist of small, translucent crystals, and on analysis gives numbers corresponding with the formula Cd_2O. *Cadmous oxide*, on further heating, breaks up into a mixture of the normal oxide and the metal, the mixture having a distinctly green colour. G. T. M.

Crystallised Basic Cupric Nitrate. By G. ROUSSEAU (*Compt. rend.*, **111**, 38—40).—The trihydrate $Cu2NO_3 + 3H_2O$ was heated with fragments of marble in sealed tubes at temperatures varying between 180° and 330° for a time varying from 24 to 48 hours. Small, thin, bluish-green tables crystallised out, identical with the rhombic plates obtained by Bourgeois (this vol., p. 714). With the

hexahydrate $Cu2NO_3 + 6H_2O$, magnificent, transparent, green prisms, as much as 5 cm. long, were obtained. They are monoclinic, and are identical with the crystals which Wells and Penfield described, but which Bourgeois was unable to obtain by their method (*loc. cit.*). Under all conditions, and with either hydrate, the crystallised basic nitrate has the composition ascribed to it by Gerhardt, $3CuO,Cu2NO_3,H_2O$, and hence it would seem that the basic nitrate of Berthelot and Graham, $3CuO,N_2O_5,H_2O$, does not exist.

C. H. B.

Mercuricobaltammonium Salts. By G. Vortmann and E. Borsbach (*Ber.*, **23**, 2803—2806; compare this vol., p. 13).—On adding a strongly alkaline solution of potassio-mercuric iodide (Nessler's reagent) to luteocobalt chloride, the compound $Co_2N_{12}H_{32}(Hg{\cdot}OH)_4I_4(OH)_2$, is obtained as a voluminous, flocculent, light brown precipitate, insoluble in water, but sparingly so in acids. A red crystalline powder with the formula $Co_2N_{12}H_{33}(HgI)_3I_6$ is formed on adding mercuric iodide solution (4 mols.) and sodium hydroxide (4 mols.) to luteocobalt chloride (1 mol.). On treating this compound with sodium hydroxide, the luteo-salt dissolves, and the bright red residue consists of $Co_2N_{12}H_{32}(HgI)_4I_6$; the same substance is also formed by the action of a large excess of sodium hydroxide on a mixture of luteocobalt chloride and mercuric iodide.

$Co_2N_{10}H_{20}(HgI)_4(Hg{\cdot}OH)_6I_6$ is obtained as a yellow precipitate on adding a little sodium hydroxide solution to a mixture of purpureocobalt chloride and potassio-mercuric iodide; it is sparingly soluble in acids, more readily in potassium iodide, and is also formed on digesting the double salt of purpureocobalt chloride and potassio-mercuric iodide with sodium hydroxide.

On adding 1—2 c.c. of a 10 per cent. solution of sodium hydroxide to roseocobaltdecamine chloride (1 gram), and potassio-mercuric iodide, a salt with the formula $Co_2N_{10}H_{27}(HgI)_3I_6$ is formed. With about 5 c.c. of the above solution of sodium hydroxide, the compound $Co_2N_{10}H_{26}(HgI)_4I_6$ is precipitated; whilst with a large excess of sodium hydroxide, a substance with the formula

$$Co_2N_{10}H_{26}(HgI)_4I_4(OH)_2$$

is obtained as a yellowish-brown powder.

$Co_2N_8H_{15}(HgOH)_6I_6$ is the only compound which could be obtained from purpureocobaltoctamine chloride.

On treating roseocobaltoctamine chloride with potassio-mercuric iodide and an equal amount of sodium hydroxide (10 per cent. solution), a brown precipitate of $Co_2N_8H_{21}(HgI)_3I_6$ is formed, soluble in nitric acid or hydrochloric acid. With 1·5—2 parts of sodium hydroxide, $Co_2N_8H_{20}(HgI)_4I_6$ is obtained; its colour is reddish brown. A brown compound with the formula $Co_2N_8H_{20}(HgI)_4I_4(OH)_2$, is formed by the action of a large excess of sodium hydroxide.

J. B. T.

Action of Potassium and Sodium Arsenates on Metallic Sesquioxides. By C. Lefèvre (*Compt. rend.*, **111**, 36—38; compare this vol., p. 562).—*Alumina.*—Potassium metarsenate with 6 to 7 per

cent. of the oxide yields a pyroarsenate, $2Al_2O_3,3As_2O_5$, in small, colourless, transparent prisms, which have longitudinal extinctions and two very widely separated axes. With more than 7 per cent. of alumina, the product is an arsenate, $2Al_2O_3,3K_2O,3As_2O_5$, analogous to the phosphate formed under similar conditions; it crystallises in colourless, striated lamellæ, with longitudinal extinctions. The addition of 20 per cent. of potassium chloride to the mixture promotes the crystallisation of this compound, but a higher proportion yields an almost amorphous product.

Potassium pyroarsenate and orthoarsenate, with sufficient potassium chloride to give a fluid mass, yield only amorphous products.

Sodium metarsenate yields the compound $2Al_2O_3,3As_2O_5$, but with more than 8 per cent. of alumina the compound $2Al_2O_3,3Na_2O,3As_2O_5$ is also obtained, and the latter is the sole product if about 20 per cent. of sodium chloride is present. It forms transparent lamellæ with longitudinal extinctions. With a large proportion of sodium chloride, or with the pyro- and ortho-arsenate, the results are similar to those obtained with the potassium salts.

Chromic Oxide.—The results are precisely similar to those obtained with alumina, and the products are $2Cr_2O_3,3As_2O_5$, which forms transparent, green prisms, sometimes elongated, sometimes flattened, with oblique extinctions; $2Cr_2O_3,3K_2O,3As_2O_5$, which separates in macled, transparent, green prisms, which show longitudinal extinctions and are probably monoclinic; and $2Cr_2O_3,3Na_2O,3As_2O_5$, which crystallises in transparent, green, rhomboidal dodecahedra.

Ferric Oxide.—Potassium metarsenate and about 7 per cent. of the oxide yield the pyroarsenate, $K_2O,Fe_2O_3,2As_2O_5$, in colourless, transparent, rhombic prisms, which act strongly on polarised light. Sodium metarsenate yields the salt, $Na_2O,Fe_2O_3,2As_2O_5$, in greenish, transparent prisms. In other respects, the results are analogous to those obtained with alumina and chromic oxide. The compound $2Fe_2O_3,3K_2O,3As_2O_5$ forms large, greenish, strongly macled lamellæ, and the compound $2Fe_2O_3,3Na_2O,3As_2O_5$ forms transparent, green, monoclinic prisms. C. H. B.

Chromiodates. By A. Berg (*Compt. rend.*, **111**, 42—43).—The author has previously described (Abstr., 1887, 776) chromiodic acid and its potassium, sodium, ammonium, and lithium salts, the potassium compound being identical with the product obtained by Blomstrand (this vol., p. 107). He has also prepared several other salts. *Magnesium chromiodate*, obtained in somewhat brownish-red, crystalline crusts by treating magnesium oxide or carbonate with excess of chromic acid, and then adding two molecular proportions of iodic acid for each molecular proportion of magnesium oxide. *Cobalt chromiodate*, obtained in a similar manner, has a similar appearance, but if kept for a long time over sulphuric acid, it loses water, and yields a violet-brown, crystalline powder. *Nickel chromiodate* is obtained in a similar manner in well-developed, brownish-yellow crystals, which seem to contain 3 mols. H_2O. The *silver salt* cannot be obtained in the same way, because silver iodate separates. Silver nitrate is dissolved in nitric acid, and chromic anhydride (1 mol.) is

added. Silver chromate separates, and powdered iodic acid (1 mol.) is then added, and the liquid boiled until the chromate is changed into the paler chromiodate, which is washed with alcohol and recrystallised from boiling nitric acid. It forms a brilliant, crystalline, bright-red powder of the composition $AgO{\cdot}CrO_2{\cdot}O{\cdot}IO_2$, and is only slightly attacked by cold water, but is rapidly decomposed by boiling water. The *copper salt* is obtained in the same way, and is very soluble in boiling nitric acid, from which it separates in yellowish-brown, soft crystals on cooling. Slow concentration of the nitric acid solution yields larger crystals, and if they are gently heated they lose water and acquire a cinnabar-red colour. When exposed to air, the copper salt absorbs water and decomposes, and if treated with water it at once splits up into chromic acid and cupric iodate. C. H. B.

Double Phosphates of Tin, Titanium, and Copper. By L. OUVRARD (*Compt. rend.*, **111**, 177—179; compare this vol., p. 1055).—*Titanium dioxide*, with a large excess of potassium metaphosphate, yields cubo-octahedrons of the phosphate TiO_2,P_2O_5, identical with those obtained by Hautefeuille and Margottet by the action of phosphoric acid. With a higher proportion of titanic oxide, the phosphate $K_2O,4TiO_2,3P_2O_5$ is obtained in small, highly refractive, almost cubic crystals, isomorphous with the corresponding sodium salt. Potassium pyrophosphate or orthophosphate yields a basic salt, $K_2O,2TiO_2,P_2O_5$, in biaxial crystals, probably monoclinic, but closely resembling regular octahedra. With other proportions of titanic oxide, acicular crystals of rutile are obtained, and these crystals are formed instead of the double phosphate if an excess of potassium chloride is present. Sodium metaphosphate gives the phosphate described by Wunder, $Na_2O,4TiO_2,3P_2O_5$, in highly birefractive rhombohedra of 91° 22′, with diagonal extinctions. The phosphate obtained by Knop under these conditions, TiO_2,P_2O_5, was also obtained, and with other proportions, acicular crystals of rutile were formed, but, contrary to the statement of Rose, no anatase. Sodium pyrophosphate or orthophosphate yields the salt $6Na_2O,3TiO_2,4P_2O_5$, in macled, striated prisms, with longitudinal extinctions.

Stannic oxide, with potassium metaphosphate, yields the salt $K_2O,4SnO_2,3P_2O_5$, isomorphous with the corresponding titanium compound. No cassiterite is obtained. Potassium pyrophosphate or orthophosphate yields crystals of the salt $K_2O,2SnO_2,P_2O_5$, similar to those of the analogous titanium compound, but more highly birefractive. With sodium metaphosphate, the author obtained the salts $Na_2O,4SnO_2,3P_2O_5$ and Na_2O,SnO_2,P_2O_5, described by Wunder, and SnO_2,P_2O_5, described by Knop, but not the salt $2SnO_2,P_2O_5$, obtained by the latter.

Cupric oxide or carbonate, with potassium metaphosphate, yields large, greenish-blue, probably monoclinic lamellæ of the salt $K_2O,8CuO,3P_2O_5$. Potassium pyrophosphate yields the compound $K_2O,2CuO,P_2O_5$, in pale-blue crystals with oblique extinctions. Potassium orthophosphate yields the same salt together with some crystals of cuprite if the proportion of cupric oxide is considerable. Sodium metaphosphate yields, as Wallroth has already stated, dichroic prisms,

probably monoclinic, of the salt $3Na_2O,3CuO,2P_2O_5$. With an excess of cupric oxide, or with sodium pyrophosphate, the salt $Na_2O,2CuO,P_2O_5$ is obtained in prisms with oblique extinctions. Sodium orthophosphate produces a mixture of cupric and cuprous oxides, together with amorphous matter.

Titanic, stannic, and cupric oxides are characterised by double phosphates of the formulæ $Na_2O,4MO_2,3P_2O_5$ and $6Na_2O,3MO_2,4P_2O_5$.

C. H. B.

Arsenovanadic Acids. By C. FRIEDHEIM and W. SCHMITZ-DUMONT (*Ber.*, **23**, 2600—2608; compare this vol., p. 1066).—The compound prepared by Berzelius by oxidising vanadyl arsenate, $V_2O_4,2As_2O_5 + 3H_2O$, with nitric acid, is identical with the vanadium arsenate obtained by Fernandez, and has not, therefore, the composition $2V_2O_5,3As_2O_5$ assigned to it by Berzelius.

Vanadium arsenate, $V_2O_5,As_2O_5 + 10H_2O$, is also formed when a concentrated solution of arsenic acid is boiled with excess of vanadic hydrate. It gradually loses some of its water of crystallisation on exposure to the air, and, when kept over sulphuric acid or heated at 100°, about 9 mols. of water are eliminated; it is converted into the anhydrous salt at about 440° without decomposition, but aqueous solutions of a certain concentration are decomposed at 100° with elimination of vanadic hydrate; it separates from nitric acid in crystals containing 2 mols. H_2O.

Compounds of the general formula $2R''O,2V_2O_5,3As_2O_5$ can be obtained by dissolving the carbonates of the metals $R''CO_3$ in excess of vanadium arsenate and evaporating the solution over sulphuric acid. The following orange-red, crystalline salts were prepared in this way.

$$2ZnO,2V_2O_5,3As_2O_5 + 23H_2O,$$
$$2CaO,2V_2O_5,3As_2O_5 + 21H_2O,$$
$$2SrO,2V_2O_5,3As_2O_5 + 20H_2O.$$

The crystalline salts of the composition $2MgO,2V_2O_5,3As_2O_5 + 23H_2O$ and $2(NH_4)_2O,2V_2O_5,3As_2O_5 + 4H_2O$ were prepared by treating magnesium and ammonium vanadate respectively with excess of arsenic acid.

The compounds

$$ZnO,V_2O_5,As_2O_5 + 6\tfrac{1}{2}H_2O,$$
$$CuO,V_2O_5,As_2O_5 + 4H_2O,$$
$$CoO,V_2O_5,As_2O_5 + 9H_2O,$$
$$MgO,V_2O_5,As_2O_5 + 10H_2O$$

were also obtained by treating the normal vanadates with arsenic acid and by various other methods.

The salt $5(NH_4)_2O,2V_2O_5,4As_2O_5 + 19H_2O$, described by Ditte, has no existence, but the compounds $(NH_4)_2O,2V_2O_5,As_2O_5 + 5H_2O$ and $K_2O,2V_2O_5,As_2O_5 + 5H_2O$ can be easily prepared in various ways; both substances crystallise in microscopic needles, and lose the whole of their water at 100°.

F. S. K.

Thiovanadates. By G. Krüss and K. Ohnmais (*Ber.*, **23**, 2547—2552).—*Ammonium thiovanadate*, $(NH_4)_3VS_4$, is deposited in crystals when hydrogen sulphide is passed for several hours into an ice-cold saturated solution of ammonium metavanadate in ammonium hydrate of sp. gr. 0·898, and the dark-violet solution obtained in this way is kept for some days. It can be more conveniently prepared by adding a solution of ammonium hydrosulphide to a solution of potassium metavanadate or sodium pyrovanadate; after a comparatively short time, ammonium thiovanadate separates from the solution in rhombic crystals, $a : b : c = 0·9825 : 1 : 1·742$, similar in appearance to those of potassium permanganate; its sp. gr. is 1 6202.

Ammonium pyroxyhexathiovanadate, $(NH_4)_2V_2S_6O$, is formed when hydrogen sulphide is passed into a solution of ammonium metavanadate in ammonium hydrate of greater sp. gr. than 0·898; on keeping the red solution for some months at a low temperature, a considerable quantity of the salt is deposited in crystals. It is rather darker in colour than the normal salt described above, and its sp. gr. is 1·7155.

The corresponding *potassium* salt, $K_4V_2S_6O + 3H_2O$, can be prepared by treating an ice-cold solution of potassium vanadate in potash of sp. gr. 1·472 with hydrogen sulphide in absence of air; after a long time, the salt separates from the solution in crystals resembling those of freshly-prepared potassium permanganate; it has a sp. gr. of 2·1443. When carefully heated at 150°, it is converted into the anhydrous salt, but if heated too quickly, it melts to a cherry-red liquid, and, on continued heating, is decomposed with liberation of sulphur.

A salt of the composition $K_8V_4S_{12}O_2 + 3H_2O$ is obtained in large crystals when the mother liquors from the preceding compound are evaporated over phosphoric anhydride; its sp. gr. is 2·1195.

Several double salts, or mixtures of potassium and ammonium thiovanadate, were prepared by treating a solution of potassium vanadate in potash with hydrogen sulphide, and then mixing it under different conditions with a solution of ammonium thiovanadate in ammonium hydrosulphide; the analyses of these mixtures showed that they contained the normal ammonium salt, and most probably also the normal potassium salt K_3VS_4.

Sodium orthoxytrithiovanadate, $Na_3VS_3O + 5H_2O$, is deposited in crystals when a solution of sodium hydrate of sp. gr. 1·122 (30 c.c.) is saturated with hydrogen sulphide, mixed with an aqueous solution (6 c.c.) of sodium pyrovanadate (3 grams), and hydrogen sulphide passed through the ice-cold mixture for four hours; it forms small, dark reddish-brown, very deliquescent crystals, and gradually loses the whole of its water when heated.

Sodium orthoxythiovanadate, $Na_3VSO_3 + 10H_2O$, is precipitated as an oil when freshly-prepared sodium hydrosulphide is added to a boiling solution of sodium pyrovanadate, the mixture boiled for a short time, and the ice-cold, filtered solution treated with alcohol (3 vols.); after being repeatedly washed with cold alcohol, it solidifies to a mass of orange-red crystals. It melts at 18°, and its sp. gr. is 1·7727.

F. S. K.

Rhodium Nitrites. By E. LEIDIÉ (*Compt. rend.*, **111**, 106—109). —A solution of rhodium chloride or of rhodium potassium chloride is slightly acidified with hydrochloric acid, diluted until it contains not more than 5 grams of rhodium per litre, heated to boiling, and mixed with successive small quantities of potassium nitrite until the solution is decolorised, and a slight turbidity appears. The liquid is allowed to cool, and the crystals which separate are washed with cold water and dried at 105°.

The potassium rhodium nitrite thus obtained, $Rh_2(NO_2)_6,6KNO_2$, forms white, microscopic crystals which do not act on polarised light; it is almost insoluble in cold water, only slightly soluble in boiling water, and quite insoluble in alcohol, in a solution containing an excess of potassium nitrite, and in a 30 per cent. solution of potassium chloride, or a 50 per cent. solution of potassium acetate. It is slowly decomposed by cold concentrated mineral acids, and more rapidly on heating. With hydrochloric acid, it yields the double chloride $Rh_2Cl_6,6KCl + 3H_2O$, obtained by Claus, but if this is treated with potassium chloride, it is converted into the salt $Rh_2Cl_6,4KCl$, which is more stable, and which is the only double salt formed by the crystallisation of a mixed solution of potassium and rhodium chlorides.

The sodium salt is analogous in composition, and is prepared in a similar manner, but the solution must be mixed with an equal volume of alcohol of 90°. It forms white, somewhat bulky crystals, which act on polarised light. It dissolves in 2·5 parts of water at 17°, and in 1 part of boiling water, but is insoluble in alcohol. An aqueous solution of the salt does not give the ordinary reactions of rhodium; it yields no precipitate with sodium hydroxide or carbonate, and with potassium or ammonium hydroxide or carbonate no precipitate of rhodium oxide is formed, but the insoluble potassium rhodium or ammonium rhodium nitrite separates. Hydrogen sulphide or sodium sulphide will, however, precipitate rhodium sulphide, slowly in the cold, more rapidly on heating. The sodium salt is readily attacked by mineral acids, especially on heating, and with hydrochloric acid it yields the chloride $Rh_2Cl_6,6NaCl + 18H_2O$.

The ammonium salt cannot be prepared directly in consequence of the ready decomposition of ammonium nitrite, but it is obtained by adding ammonium chloride to a solution of the sodium salt. It separates in white, microscopic crystals which have no action on polarised light. In solubility and behaviour towards acids it is precisely similar to the potassium salt; with hydrochloric acid, it yields the salt $Rh_2Cl_6,6NH_4Cl + 3H_2O$.

The barium salt, $Rh_2(NO_2)_6,3Ba(NO_2)_2 + 12H_2O$, is obtained in the same way as the sodium and potassium compounds, and separates in somewhat bulky, white crystals, soluble in 50 parts of water at 16°, and in 6·5 parts of boiling water. The crystals have no action on polarised light. With hydrochloric acid, the salt yields a mixture of rhodium and barium chlorides, which, however, will not form a double salt, and if the barium is precipitated by sulphuric acid, the rhodium chloride can be obtained quite free from alkaline chlorides. A solution of barium rhodium nitrite behaves towards potassium

and ammonium salts like the double sodium nitrite; with sodium hydroxide or carbonate, a precipitate of the corresponding barium compound is obtained, but all the rhodium remains in solution in the form of the double sodium salt.

The insolubility of potassium rhodium nitrite can be utilised for the preparation of pure rhodium, its separation from other metals of the platinum group, and its quantitative estimation.

C. H. B.

Double Salts of Rhodium. By K. Seubert and K. Kobbé (*Ber.*, **23**, 2556—2561).—Potassium rhodium chloride, $Rh_2Cl_6,4KCl + 2H_2O$, is deposited in deep-red crystals when spongy rhodium (1 part) is fused with potassium chloride (2 parts) in a stream of chlorine, and the filtered aqueous solution of the product evaporated under reduced pressure. If the mother liquors are then saturated with hydrogen chloride to precipitate the potassium chloride and the filtered solution again evaporated, a new salt is obtained in dark-red, sparingly soluble crystals, which become cloudy and lighter in colour when kept over phosphoric anhydride, and have then the composition $Rh_2Cl_6,6KCl + 3H_2O$.

Sodium rhodium sulphite, $4RhSO_3,6Na_2SO_3 + 9H_2O$, is obtained when a solution of rhodium chloride is heated for some time with excess of sodium hydrogen sulphite, the precipitate washed with cold water and dried over phosphoric anhydride. It is only very sparingly soluble in hot water, but it dissolves freely in nitric acid with evolution of sulphurous anhydride.

Sodium rhodium sulphate has been previously obtained by Bunsen (*Annalen*, **146**, 265), by heating the sulphite just described with concentrated sulphuric acid; it has the composition $Rh_2(SO_4)_3,Na_2SO_4$.

F. S. K.

Iridium Phosphorus Bromides. By G. Geisenheimer (*Compt. rend.*, **111**, 40—41).—1 gram of hydrated iridium dioxide is mixed with 10 grams of bromide, and phosphorus tribromide added gradually until the whole mass becomes solid. The tube is then sealed and heated for two to three hours at 150°; the hydrobromic acid is allowed to escape, the tube is re-sealed and then heated for 24 hours at 300°. A deep-red liquid is thus obtained which solidifies in confused red and yellow crystals. The tube is now heated in a vertical position for two to three hours at 100°, and is gradually inverted in order to separate the liquid from the red crystals, which are washed with boiling carbon bisulphide; they are red needles and have the composition $Ir_2Br_6,6PBr_3$.

When treated with water they are partially attacked and yield an acid solution and a black substance with a red lustre, which is soluble in water with difficulty and has the same composition as the original crystals. If the compound is heated with phosphorus tribromide in sealed tubes at 200° it yields the compound $Ir_2Br_6,4PBr_3$ in black crystals, and it follows that excess of the tribromide should be avoided in the preparation of the first substance.

Attempts to obtain a bromine compound analogous to $Ir_2P_6Cl_{24}$ gave negative results. When the bromide, $Ir_2P_6Br_{24}$, is heated in

sealed tubes with bromine, it yields phosphorus pentabromide and the compound $Ir_2P_4Br_{18}$. A mixture of phosphorus pentabromide, the compound $Ir_2P_6Br_{24}$, and phosphorus oxychloride behaves in a similar manner. If the chloride $Ir_2P_5Cl_{30}$ is heated at 300° with PBr_3, it yields only a mixture of the chloride $Ir_2P_6Cl_{24}$, the bromide $Ir_2P_4Br_{18}$, and phosphorus chlorobromide. If, however, a mixture of the bromide $Ir_2P_6Br_{24}$, phosphorus pentabromide, and phosphorus trichloride is heated, a compound $Ir_2Br_8,4PCl_3$ is obtained, and this indicates the possible existence of a perbromide.

The difficulty experienced in preparing the higher bromides is probably due partly to the reducing action of the phosphorus tribromide, observed by Lindet in the cause of gold phosphorus perbromide, and partly to the instability of phosphorus pentabromide.

The iridium phosphorus chlorides and bromides differ in that the most stable chloride has the composition $Ir_2P_6Cl_{24}$, and the most stable bromide the composition $Ir_2P_4Br_{18}$.

The author has analysed the acid $Ir_2Br_6,6H_3PO_3$ and its potassium and lead salts. C. H. B.

Mineralogical Chemistry.

Artificial Production of Boracite in the Wet Way. By A. DE GRAMONT (*Compt. rend.*, 111, 43—44).—1 part of sodium borate, 2 parts of magnesium chloride, and a small quantity of water are heated in sealed tubes at 275—280°. The product, after being separated by levigation from the amorphous magnesium borate, is a white, crystalline powder, which scratches glass. It consists of microscopic birefractive tetrahedra, cubo-tetrahedra, and pyramidal tetrahedra; sp. gr. = 2·89, that of the natural mineral being 2·90. The composition of the product agrees closely with that of natural boracite and is as follows:—MgO, 27·26; B_2O_3 (calc.), 63·86; Cl, 7·71; Mg, 2·60 = 101·43. C. H. B.

Normal Aluminium Sulphate. By P. M. DELACHARLONNY (*Compt. rend.*, 111, 229—231).—The author has examined some finely-crystallised specimens of native aluminium sulphate from Bolivia. They were covered with a white, amorphous crust, but the interior consisted of translucent, prismatic crystals of the composition $Al_2(SO_4)_3 + 16H_2O$, and are, therefore, identical in their degree of hydration with the artificial product (Abstr., 1884, 820).

C. H. B.

Meteoric Iron from Magura, Hungary. By BERTHELOT and FRIEDEL (*Compt. rend.*, 111, 296—300).—The meteoric iron examined weighed 280 grams, and was obtained from Magura, in Arva, Hungary. In order to ascertain whether it contained any diamonds, it was repeatedly treated with aqua regia, and the matter remaining

undissolved was treated with nitric acid and potassium chlorate. After combustion of the graphitic acid, there was left a small quantity of a white, crystalline powder, which scratched rubies. It did not disappear on treatment with ammonium fluoride and sulphuric acid, and did not burn when heated under such conditions that small fragments of diamond burnt away completely. Optical examination and determination of the sp. gr. showed that the substance had all the properties of quartz.

C. H. B.

Mineral Waters of Cransac (Aveyron). By A. Carnot (*Compt. rend.*, **111**, 192—195).—These springs rise in the Valley of Cransac below the outcrop of beds of coal surmounted by carbonaceous schists containing pyrites. They do not rise from any great depth, but must be regarded as rain water which has come in contact with mineralising strata comparatively near the surface. The following table gives the quantities of the various compounds per litre :—

	Fraysse 1.	Fraysse 2.	Valette.	Galtié.	Euphie. Galtié.	Haute Albagnac.	Basse Albagnac.	Roques.	Rouquette.
SiO_2	0·0250	0·0460	0·0300	0·0240	0·0062	0·0032	0·0032	0·0620	0·0320
$CaCO_3,CO_2$	0·0000	0·0000	0·0720	traces	0·0144	0·0315	0·0093	traces	traces
$CaSO_4$	0·2757	0·6970	0·1156	0·8959	0·5950	0·5219	0·3604	1·0850	0·3910
$MgSO_4$	0·4215	1·3113	0·2994	0·3120	0·4830	0·4470	0·2745	1·2460	0·3600
$Al_2(SO_4)_3$	0·0087	0·2790	0·0000	0·0000	0·0000	0·0000	0·0000	0·0300	0·0230
$Fe_2(SO_4)_3$	0·0017	0·0087	0·0025	0·0025	0·0025	0·0025	0·0025	traces	traces
$MnSO_4$	0·0127	0·1550	0·0019	0·0019	0·0038	traces	absent	0·0610	0·0197
$Ca(NO_3)_2$	0·1435	0·0000	0·5380	0·2020	traces	0·2566	traces	0·0000	0·0000
KNO_3	0·3574	0·1720	0·0205	0·0272	0·0228	0·0160	0·0119	0·0300	0·1950
NaCl	0·0778	0·0270	0·1044	0·0208	0·0626	0·0464	0·0278	0·0250	0·0990
LiCl	traces	traces	traces	traces	traces	traces	traces	traces	traces
Total	1·3240	2·6960	1·1843	1·4863	1·1903	1·3251	0·6896	2·5390	1·1197

Carbonates are present in very small quantities, but sulphates exist in large proportions. The sulphuric acid is doubtless derived from pyrites, but the iron has been almost entirely removed by the passage of the water over magnesium limestones. The nitrates are probably derived from ammonium compounds produced from the coal by the action of the subterranean fires which are known to occur in the district.

C. H. B.

Organic Chemistry.

Hydrates of Gases. By VILLARD (*Compt. rend.*, **111**, 302—305).—Propane was purified from air and hydrogen by liquefying the gas and then opening the reservoir at the top. The air and hydrogen escaped, and when the liquid propane had risen to the aperture, the pressure inside the apparatus was made to coincide with the atmospheric pressure, and the aperture was sealed up.

In order to obtain the propane hydrate, part of the tube must be momentarily cooled below 0°; crystals separate and continue to form at temperatures higher than 0°, until all the liquid propane has disappeared. The tension of dissociation of the hydrate at 0° is about 1 atmos., but it can be preserved indefinitely under suitable pressure at temperatures below 8·5°. At 8·5°, it decomposes, whatever the pressure, and this temperature is not altered by the presence of air. It is noteworthy that, in the methane series, the critical temperature of the formation of the hydrates is lower, the higher the molecular weight of the hydrocarbon.

Carbon fluorides form hydrates under similar conditions, the critical temperatures being as follows: carbon tetrafluoride, +20·4°; carbon difluoride, +10·5°; methylene fluoride, +17·6°; and trifluoromethane, +21·8°. C. H. B.

Hydrates of Haloïd Alkyl Salts. By VILLARD (*Compt. rend.*, **111**, 183—185).—The hydrates were formed under the same conditions as the hydrate of methyl chloride (Abstr., 1888, 644 and 897). The hydrate of ethyl fluoride can be kept under pressure at the ordinary temperature for many hours; hydrate of methyl fluoride decomposes at 18·8°; hydrate of ethyl chloride forms acicular crystals, 2 or 3 mm. long, which decompose at 5°, even under a pressure of 2 atmos., and the hydrate of methyl iodide also decomposes at 4·8°.

The following tables give the tension in atmospheres of the hydrates of the alkyl fluorides.

Hydrate of Ethyl Fluoride.

$t°$	0°	2°	3·7°	5·2°	12·5°	15·5°	18·0°
p	0·7	0·9	1·0	1·3	4	5	7

Hydrate of Methyl Fluoride.

$t°$	0°	5·3°	8·5°	10·4°	13·2°	14·2°	15·8°
p	2·1	3·5	5·5	7·5	12·5	15·0	19·5

C. H. B.

Geometrical Isomerides of the Hexamethylene Derivatives. By H. SACHSE (*Ber.*, **23**, 1363—1370).—Starting from the hypotheses that the four affinities of a carbon atom are directed from the centre to the solid angles of a regular tetrahedron, and that two carbon atoms which are united by a single bond will tend so to place themselves that the directions of the two combining affinities fall in one

and the same straight line, the author comes to the conclusion that, although in rings of three, four, or five carbon atoms, the centres of the tetrahedra may all lie in the same plane, this is no longer possible with rings containing a larger number of carbon atoms. In the case of hexamethylene, if the centres of contiguous carbon atoms be united by straight lines, then a broken line in space will thus be formed. According to the conditions of the above hypotheses, this broken line must consist of six straight lines, equal in length, and which meet each other at angles of 109° 28′. These conditions, which lead to a system of three equations, can be satisfied by two different configurations, which are found to resemble and bear a very simple relation to the configuration of the benzene molecule formerly described by the author (Abstr., 1888, 1181). By the aid of the formulæ thus arrived at, the isomerism which has been observed in the case of the hexahydromellitic and the hexahydroterephthalic acids may be easily explained and represented. H. C.

Nitroprussides. By PRUD'HOMME (*Compt. rend.*, **111**, 45—46).—When an aqueous solution of an alkaline nitrite and an alkaline ferricyanide is boiled, the latter salt is partially converted into a nitroprusside. By using the azosulphonates (obtained by the action of sodium nitrite on sodium hydrogen sulphite), very concentrated solutions of nitroprussides can be obtained. 34·5 grams of sodium nitrite, dissolved in 150 grams of water at 70°, is mixed with 216 grams of sodium hydrogen sulphite of 37° B. and a solution of 82 grams of potassium ferricyanide in 250 grams of water at 70°. The mixture is boiled until evolution of gases ceases, and the cooled liquid, which already contains much nitroprusside, is gradually mixed with 54 grams of sodium hydrogen sulphite of 37° B. The deep red liquid thus obtained contains a very large quantity of the nitroprusside. With the same quantity of nitrite, the yield varies with the proportions of sulphite and ferricyanide. The results are also different if the first stage of the operation is conducted at a low temperature. Under these conditions, if a sufficient quantity of sulphite is present, no nitrogen oxides are evolved. With proportions of sulphite and ferricyanide slightly different from those given, the solution of nitroprusside, after a time, deposits white, silky crystals, only very slightly soluble in water. They frequently decompose whilst in a moist state on the filter, and are at once decomposed by boiling water into Prussian blue and sulphuric acid. They seem to be identical with the product obtained by dissolving Prussian blue in concentrated sulphuric acid.

If an aqueous solution of 34·5 parts of sodium nitrite, 15·5 parts of sodium thiosulphate, and 41 parts of potassium ferricyanide is boiled, the ferricyanide is gradually converted into nitroprusside, the yield of the latter being greater than if the thiosulphate were not present. The liquid also deposits a brown substance, which dissolves in concentrated hydrochloric acid, and if water is added to this solution, Prussian blue is precipitated, and the liquid contains ferric chloride.

When a nitroprusside is added to the yellow solution obtained by

boiling sulphur with sodium hydroxide solution of 36° B., a beautiful dichroic solution is obtained, purple by transmitted light, and blue by reflected light. C. H. B.

Tertiary Butyl Carbinol. By M. FREUND and F. LENZE (*Ber.*, **23**, 2865—2869).—*Trimethylacetamideoxime*, $CMe_3\cdot C(NH_2)\colon NOH$, is prepared from trimethylacetonitrile, and melts at 115—116°; the corresponding *phenylamidine oxalate* melts at 192°. *Tertiaryamylamine*, $CMe_3\cdot CH_2\cdot NH_2$, is formed by the reduction of the nitrile with sodium in alcoholic solution; it boils at 82—83°, and rapidly absorbs carbonic anhydride on exposure to the air. The *platinochloride* crystallises in pale-yellow plates; the *aurochloride* is deposited in lemon-yellow needles. *Amylcarbamide*, $CMe_3\cdot CH_2\cdot NH\cdot CO\cdot NH_2$, is obtained by the action of potassium cyanate; it crystallises from ether in small needles melting at 145°. *Phenylamylcarbamide*,

$$CMe_3\cdot CH_2\cdot NH\cdot CO\cdot NHPh,$$

crystallises from alcohol in white needles, which melt at 155°. *Phenylamylthiocarbamide*, $CMe_3\cdot CH_2\cdot NH\cdot CS\cdot NHPh$, melts at 136°. *Diamyloxamide*, $CMe_3\cdot CH_2\cdot NH\cdot CO\cdot CO\cdot NH\cdot CH_2\cdot CMe_3$, is formed by the action of ethyl oxalate on the amine; it crystallises from ether in needles melting at 165°. *Tertiary butyl carbinol*, $CMe_3\cdot CH_2\cdot OH$, is prepared by the action of silver nitrite on the hydrochloride of the amine; it is a colourless liquid with a camphor-like odour, has a sp. gr. of 0·8122 at 20°, boils at 102—103°, and is somewhat soluble in water. During the preparation of trimethylacetonitrile, Butlerow obtained a compound to which he gave the formula $CMe_3\cdot NH\cdot CHO$; the authors have also observed the formation of this substance, but their analyses show that it contains no oxygen. J. B. T.

Amyl Alcohol in Brandy from different parts of the German Empire. By SELL (*Ann. Agronom.*, **16**, 335—336).—The quantity varied from 0·641 to 0·016 per 100 parts of ethyl alcohol, that is, 0·256—0·006 per cent. of the brandy of commerce. J. M. H. M.

Mannitol Hexachlorhydrin. By L. MOURGUES (*Compt. rend.*, **111**, 111—113).—Mannitol is heated for several hours at a temperature not exceeding 145° with seven times its weight of phosphorus pentachloride containing a small quantity of the oxychloride. When evolution of hydrogen chloride ceases, the phosphorus oxychloride is distilled off at a temperature not exceeding 145°, and the syrupy product is gradually poured into ice-cold water, and is then distilled in a current of steam. The first portion of the distillate contains a mixture of chlorine and oxygen derivatives of mannitol and mannitan, after which mannitol hexachlorhydrin, $C_6H_8Cl_6$, passes over. It crystallises in odourless, small, white, nacreous leaflets, which melt and volatise at 137·5°. It boils at 180—185° under a pressure of 30 mm., and is insoluble in water, slightly soluble in alcohol, and very soluble in ether, benzene, chloroform, light petroleum, &c. Its sp. gr. is 2·060, and its rotatory power in a benzene solution at 20° is $[\alpha]_D = +18° 32'$. It is not dissolved by boiling concentrated alkalis, but dissolves in

hot sulphuric acid, from which it separates on cooling. The molecular weight as determined by Raoult's method agrees with the formula $C_6H_8Cl_6$, and there is little doubt that the compound has the constitution $CH_2Cl{\cdot}[CHCl]_4{\cdot}CH_2Cl$. C. H. B.

Conversion of Glucose into Sorbite. By J. MEUNIER (*Compt. rend.*, **111**, 49—51).—Glucose is dissolved in twice its weight of water, and mixed with excess of sodium amalgam containing 2·5 per cent. of sodium, great care being taken to avoid a rise of temperature. The liquid is acidified with sulphuric acid, neutralised with barium carbonate, filtered, concentrated, and mixed with alcohol, in order to precipitate sodium sulphate, and the concentrated alcoholic filtrate is mixed with hydrochloric acid and benzaldehyde. Sorbite separates in the form of its dibenzoic acetal. If the acid and the benzaldehyde are not added in excess, the acetal separates chiefly in the soluble form (this vol., p. 731), but if excess of the reagents is employed, the greater part of the acetal is insoluble.

If the glucose is dissolved in four or five times its volume of water, and the sodium hydroxide which is formed is continually neutralised by the addition of sulphuric acid, only a very small quantity of sorbite is obtained. C. H. B.

Hydrogenation of Sorbin and the Oxidation of Sorbite. By C. VINCENT and DELACHANAL (*Compt. rend.*, **111**, 51—53).—If a 33 per cent. solution of sorbin is mixed with successive small quantities of sodium amalgam containing 2 per cent. of sodium, care being taken to avoid a very great rise of temperature, the sorbin is converted into sorbite, which can be isolated in the form of its dibenzoic acetal after neutralisation with sulphuric acid and the precipitation of the sodium sulphate by alcohol.

When sorbite is oxidised by heating it with bromine-water at 60° in a sealed tube, it yields a glucose which can be isolated in the form of a phenylglucazone, but the authors have not yet determined whether it is dextrose or levulose. C. H. B.

Optical Isomerides of Grape-sugar, Gluconic Acid, and Saccharic Acid. By E. FISCHER (*Ber.*, **23**, 2611—2624; compare this vol., pp. 466, 1223, and 1230).—l-Mannonic acid (arabinosecarboxylic acid) can be partially converted into the optically isomeric l-gluconic acid by heating it with quinoline, just as d-mannonic acid can be transformed to a certain extent into gluconic acid; l-gluconic acid, on reduction, yields l-glucose, the optical isomeride of grape-sugar, and both compounds, on oxidation with nitric acid, are converted into l-saccharic acid.

The members of the l-series resemble the known compounds of the d-series very closely, and combine with them to form the corresponding inactive substances, namely i-glucose, i-gluconic acid, and i-saccharic acid.

l-Gluconic acid is most conveniently prepared from arabinose in the following manner:—A solution of arabinose (50 grams) in warm

water (55 grams) is treated with hydrogen cyanide (10 grams), as described by Kiliani (Abstr., 1887, 229), the crystalline amide which separates from the solution in the course of three to eight days is boiled with crystalline barium hydroxide (100 grams) and water (250 grams) until the evolution of ammonia ceases, and the barium is then exactly precipitated with sulphuric acid. On evaporating the solution, previously decolorised with animal charcoal, to a thick syrup, the greater part of the l-mannonic acid separates in the form of the lactone; the mixture is agitated with a little 96 per cent. alcohol, filtered, and the residual lactone washed repeatedly with a little cold alcohol and then purified by recrystallisation from the hot solvent. The alcoholic filtrate and washings are evaporated on the water-bath, the l-mannolactone, which is deposited in the course of one to two days, separated as before, and the alcoholic liquors again evaporated. The syrup obtained in this way contains the whole of the l-gluconic acid and small quantities of l-mannonic acid; it is dissolved in water (4 parts) and warmed for an hour with phenylhydrazine (1 part) and 50 per cent. acetic acid (0·75 part); on cooling, a mixture of the two hydrazides separates from the solution in yellow crystals. This precipitate is separated by filtration, washed with cold water, alcohol, and ether consecutively, and then decomposed with barium hydroxide; the solution, freed from phenylhydrazine and barium in the usual way, is decolorised with animal charcoal, concentrated by evaporation, boiled with calcium carbonate until neutral, and then treated again with animal charcoal. The mixture of the two calcium salts which remains when the solution is evaporated is dissolved in a little hot water, and alcohol added until a turbidity is produced; on cooling, the calcium salt of l-gluconic acid is deposited as a syrup which gradually solidifies, and can then be obtained in a pure condition by recrystallisation from warm water. Having once obtained crystals of the pure calcium salt, it is unnecessary to purify the acid by means of its hydrazide; the crude syrup which is left after separating the l-mannolactone as completely as possible is dissolved in water, the boiling solution neutralised with calcium carbonate, decolorised with animal charcoal, and a small quantity of the crystalline calcium salt introduced into the concentrated solution; after a few days, a large quantity of calcium gluconate is deposited in crystals, and the salt can then be further purified by recrystallisation from warm water. 50 grams of arabinose yield 8 to 9 grams of pure calcium l-gluconate, together with about 20 grams of pure l-mannolactone.

When an aqueous solution of l-gluconic acid, obtained by decomposing the calcium salt with the theoretical quantity of oxalic acid, is boiled, the acid is partially converted into the lactone, and, on evaporating, the two compounds remain as a syrup from which crystals have not yet been obtained; the aqueous solution of this syrup is levo-rotatory. The *calcium* salt, $(C_6H_{11}O_7)_2Ca$, separates from hot water in cauliflower-like crystals, similar in appearance to those of calcium d-gluconate; it is soluble in 3 to 4 parts of hot water, and its specific rotatory power is $\alpha_D^{20°} = -6·64°$. A *basic* salt is formed when calcium hydroxide is added to a lukewarm aqueous solution of the neutral salt; on cooling the filtered solution, it is deposited in a

flocculent condition. The barium, strontium, and cadmium salts are readily soluble in water, and have not yet been obtained in crystals.

The *hydrazide*, $C_6H_{11}O_6 \cdot N_2H_2Ph$, crystallises from hot water in small, colourless plates or prisms, and when quickly heated melts at about 200° with decomposition.

l-Gluconic acid can be most readily distinguished from d-gluconic acid by converting both compounds into the corresponding lactones, and then submitting the solutions to an optical examination; the acid is best identified by converting it into l-saccharic acid in the manner described below.

l-Mannonic acid can be detected in presence of l-gluconic acid by reducing the sample with sodium amalgam, and treating with phenylhydrazine the cold, concentrated aqueous solution of the sugar produced; if l-mannose is present, even in small quantity, the hydrazone is precipitated in crystals in a few hours' time.

l-Gluconic acid is formed, as has been stated above, when l-mannonic acid is heated with quinoline at 140° for an hour, but this method is not suitable for the preparation of the acid; a large quantity of mannonic acid remains unchanged, and the gluconic acid is not easily obtained in a pure condition. l-Gluconic acid, under the same conditions, is partially converted into l-mannonic acid.

i-Gluconic acid has properties similar to those of its components; on evaporating its aqueous solution, there remains a colourless syrup which consists of a mixture of acid and lactone. The *calcium* salt, $(C_6H_{11}O_7)_2Ca$, is deposited in crystals when a solution of equivalent parts of calcium d- and l-gluconate is slowly evaporated on the water-bath; when dried at 100°, it seems to contain 1 mol. H_2O. It is soluble in 16 to 20 parts of boiling water, and, like the acid and the lactone, is optically inactive. The *hydrazide*, $C_6H_{11}O_6 \cdot N_2H_2Ph$, can be obtained by heating the acid or the calcium salt with phenylhydrazine acetate; it separates from hot water in colourless crystals, melts at 188—190°, and is optically inactive.

i-Gluconic acid can also be obtained by heating i-mannonic acid with quinoline, but the change, as in the case of the other acids, is only a partial one.

l-Glucose, $C_6H_{12}O_6$, is obtained when l-glucolactone is reduced with sodium amalgam, and the solution freed from sodium salts in the usual manner; on evaporating the alcoholic solution of the sugar, there remains a syrup which gradually crystallises. It is recrystallised from water, spread on a porous plate, then dissolved in hot methyl alcohol, and the solution mixed with alcohol; after a long time, the pure compound separates from the solution in anhydrous, prismatic crystals. It resembles grape-sugar very closely in appearance, melts at 141—143°, has a sweet taste, and is very readily soluble in water, but very sparingly in alcohol. It also resembles grape-sugar in optical behaviour, and exhibits the phenomenon of multirotation; after 12 hours' time, the rotation has become constant, the specific rotatory power being then about $\alpha_D = -51 \cdot 4°$.

Phenylhydrazine acetate produces no precipitate in a cold aqueous solution of l-glucose, but on warming, the separation of l-phenylglucosazone quickly commences.

l-Glucosediphenylhydrazone, $C_6H_{12}O_5{:}N_2Ph_2$, is formed when a solution of the sugar in dilute alcohol is heated with diphenylhydrazone ($1\frac{1}{2}$ parts) for two hours at 100°. It crystallises from hot water in slender, colourless needles, and is only very sparingly soluble in cold water; it resembles the corresponding derivative of grape-sugar, and both compounds have the same melting point (162—163°).

l-Glucose, like l-mannose and l-fructose, seems not to ferment with yeast.

i-Glucose can be obtained by mixing solutions of d- and l-glucose, or by reducing i-gluconic acid with sodium amalgam. It is a colourless syrup, very readily soluble in water, but only very sparingly in alcohol, and it shows all the reactions of its components. It does not give a precipitate with phenylhydrazine acetate in the cold, but on warming, i-glucosazone is quickly deposited from the solution.

i-Glucosediphenylhydrazone, $C_6H_{12}O_5{:}N_2Ph_2$, prepared as described in the case of the corresponding l-derivative, separates from hot water as an oil, and then gradually solidifies to a mass of colourless, crystalline plates melting at 132—133°.

A solution of i-glucose enters into brisk fermentation with yeast; after keeping the mixture for 24 hours at 30°, fermentation is at an end, and the solution is then strongly levo-rotatory, owing to the presence of l-glucose.

l-Saccharic acid can be prepared by oxidising l-gluconic acid with nitric acid. For this purpose, the crude syrup (5 grams) which is left after separating the l-mannolactone (see above) is heated on the water-bath with nitric acid of sp. gr. 1·15 (15 grams), the residual syrup diluted with water, the solution evaporated to free it from nitric acid, then neutralised with potassium carbonate and strongly acidified with acetic acid; on evaporating to a thin syrup, the hydrogen potassium salt, $C_6H_9O_8K$, begins to separate in crystals after some time, and is purified by washing it with cold water and then recrystallising from hot water with addition of animal charcoal. The yield is 25 to 30 per cent. of the crude gluconic acid employed. It forms small needles or prisms, and is feebly levo-rotatory. The *silver* salt, $C_6H_8O_8Ag_2$, is decomposed by boiling water. The *dihydrazide*, prepared by warming the acid or the calcium salt with phenylhydrazine acetate, crystallises in almost colourless plates, and melts at 213—214° with decomposition.

The potassium hydrogen salt of l-saccharic acid is so easily recognised that its formation in the manner described above affords the best test for l-gluconic acid; l-mannonic acid, under the same conditions, does not yield a crystalline potassium hydrogen salt.

The potassium hydrogen salt of *i-saccharic acid* separates in slender needles when a hot aqueous solution of the corresponding salts of d- and l-saccharic acid is allowed to cool slowly; it is readily soluble in hot, but only sparingly in cold water, and it has the composition $C_6H_9O_8K$. The *dihydrazide* of the acid crystallises in colourless plates, and melts at 209—210° with decomposition.

i-Saccharic acid can be directly obtained by oxidising i-gluconic acid with nitric acid, and isolating the product by means of its potassium hydrogen salt in the manner described above.

The potassium hydrogen salts of the two optically active saccharic acids resemble one another very closely, and are best distinguished or identified by partially converting them into the lactones by boiling with a mineral acid, and then examining the solutions optically; the corresponding salt of i-saccharic acid can be distinguished from the other two with a little practice by its appearance simply.

As the molecule of arabinose is asymmetric, assuming that no stereometric intramolecular change occurs, there may be, in accordance with Le Bel and Van't Hoff's theory, three isomeric acids formed by treating arabinose with hydrocyanic acid, namely, two acids which with respect to the asymmetric carbon atom marked in the formula

$$CH_2(OH)\cdot[CH(OH)]_3\cdot\overset{*}{C}H(OH)\cdot COOH$$

with an asterisk, possess opposite configurations, and a third, produced by a combination of the other two, into which it can, theoretically, be resolved. Two of these three acids are represented by l-mannonic acid and l-gluconic acid, either of which may be the composite isomeride. Many attempts have been made to resolve d-mannonic acid and d-gluconic acid into two isomerides, but without success, although, as has been already shown, they are mutually convertible. It seems probable, therefore, that with reference to the C* atom, gluconic acid and mannonic acid are the right and left forms respectively; as, however, they do not combine together to form a third acid, it would seem that such isomeric compounds do not always behave as is usually supposed. If so, the observations previously made on the configuration of the mannonic acids, the mannoses, and the mannitols with regard to this particular carbon atom are superfluous. All experience in the sugar group confirms the view that for every optically active substance there exists an isomeric form of opposite optical activity, and that the two compounds combine together to form an inactive modification; the last statement seems, however, to hold good only for the asymmetry of the whole molecule, and not for that of any single carbon atom. F. S. K.

Fucose, an Isomeride of Rhamnose. By A. GÜNTHER and B. TOLLENS (*Ber.*, **23**, 2585—2586).—A crystalline sugar, which the authors name *fucose*, can be isolated from the products of hydrolysis of *fucus* by means of the hydrazone (m. p. about 170°; compare this vol., p. 1105); the pure hydrazone is reconverted into the sugar by Fischer and Hirschberger's method. On evaporating a solution of the pure sugar, it is obtained in microscopic needles of the composition $C_6H_{12}O_5$; it is very readily soluble, has a sweet taste, and is levorotatory, the rotatory power being $-112°$ immediately after solution, but gradually diminishing to $-77°$. On distillation with hydrochloric acid, it gives methylfurfuraldehyde; it reduces alkaline copper solutions, and shows the general reactions of the sugars. The *osazone* melts at about 159°. F. S. K.

Trimethylenimine, and a New Synthesis of β-Picoline. By A. LADENBURG and J. SIEBER (*Ber.*, **23**, 2727—2731).—Trimethylenediamine hydrochloride was subjected to dry distillation, the distillate treated with dilute hydrochloric acid, and the solution filtered and evaporated, so that a large quantity of ammonium chloride separated out. The residue was distilled with concentrated aqueous soda, and the distillate separated by fractionation into three portions, boiling respectively at 66—70°, 140—143°, and 148—151°. From the first fraction, trimethylenimine was separated as the bismuthoiodide, $(C_3H_7N,HI)_3.2BiI_3$, by the addition of a dilute solution of bismuth and potassium iodides. This salt is red; when distilled with soda, it yields the free base which boils at 66—70°, smells like piperidine, is very hygroscopic, and mixes with water and alcohol. The *platinochloride*, $(C_3H_7N)_2,H_2PtCl_6$, forms yellow needles melting at 196°. The second fraction was shown to contain β-picoline identical with that obtained from glycerine, whilst the third fraction consisted of β′-picoline, identical with that obtained from strychnine, and which Ladenburg has shown (this vol., p. 1432) to be different from the β-picoline mentioned above. These substances were identified by means of the melting points of their platino and mercuro-chlorides, and of the nicotinic acid which they yielded when oxidised.

C. F. B.

Methylnonylphenylhydrazone. By S. GRIMALDI (*Gazzetta*, **20**, 96—98).—*Methylnonylphenylhydrazone*, $C_9H_{19}\cdot CMe\colon N_2HPh$, prepared by heating methyl nonyl ketone (from oil of rue) with phenylhydrazine, is a heavy, neutral, orange-yellow oil with an aromatic odour which remains liquid at $-5°$; sp. gr. = 0·94475 at 0°. It is insoluble in water, but dissolves in ether, carbon bisulphide, chloroform, &c. It is resinified by exposure to the air. It differs from both its constituents in having no reducing action on Fehling's solution even when heated with it.

S. B. A. A.

Derivatives of Acetylacetone. By A. COMBES (*Compt. rend.*, **111**, 272—274).—When well-cooled acetylacetone is gradually mixed with an equal molecular proportion of sulphuryl chloride, large quantities of hydrogen chloride and sulphurous anhydride are evolved, and a pungent colourless liquid is obtained which, on fractionation under ordinary pressure, boils at 156—158°. It consists of monochloracetylacetone mixed with a small quantity of the dichloro-derivative. The liquid is agitated with a concentrated solution of cupric acetate, and the compound $(C_5H_6O_2Cl)_2Cu$ separates in pale-green, silky, slender needles, which are washed with alcohol. When this compound is dissolved in dilute sulphuric acid, the solution extracted with ether, and the ether evaporated, monochloracetylacetone is obtained as a colourless, highly refractive liquid which boils at 156°, and is insoluble in water.

The monochloracetylacetone thus prepared has the constitution $CHClAc_2$, and when treated with sulphuryl chloride, yields the dichlorinated derivative CCl_2Ac_2, which boils at 87° under a pressure of 18—20 mm., and yields no metallic derivatives.

C. H. B.

Formation of Glycocine from Chloracetic Acid. By K. Kraut (*Ber.*, **23**, 2577).—It is advantageous, in preparing glycocine from chloracetic acid, to employ a very large excess of ammonium hydrate; the yield is then about 50 per cent. of the theoretical. F. S. K.

Alkyl Dicyanacetates. By A. Haller (*Compt. rend.*, **111**, 53—56).—*Ethyl dicyanacetate*, $CHCy_2 \cdot COOEt$, is obtained by adding 22 grams of ethyl cyanacetate to a solution of 4·6 grams of sodium in 100 grams of absolute alcohol, and saturating the mixture with cyanogen chloride. It combines with a small quantity of ether, and is then soluble in water and alcohol, but insoluble in ether, but if dried over anhydrous sodium sulphate and placed in a desiccator, it loses ether, and is partially converted into a gelatinous, opaque mass insoluble in water and ether, but soluble in warm alcohol. It cannot be distilled without decomposition even in a vacuum. Its aqueous solution is strongly acid and decomposes when heated, evolving carbonic anhydride and hydrogen cyanide; with silver salts, it gives a white precipitate soluble in boiling water.

Ethyl dicyanacetate is a very energetic acid, and forms salts of the type $CMCy_2 \cdot COOEt$. The sodium salt crystallises from water in slender needles, and from alcohol in large crystals, very soluble in water or alcohol; its solutions give no precipitate with ferric salts, but there is a slight red coloration which is not removed by ether. The silver salt is white and insoluble in cold water or alcohol, but dissolves in boiling water or alcohol, from which it separates in microscopic prisms. The cupric salt forms a reddish-yellow precipitate which contains 3 mols. H_2O, and is insoluble in cold water.

Methyl dicyanacetate is obtained in the same way as the ethyl compound, but its formation is always accompanied by the production of a compound, $C_6H_8N_2O_3$, insoluble in cold water, alcohol, or ether, but soluble in boiling water or alcohol, from which it crystallises in white, lozenge-shaped plates.

Methyl dicyanacetate is also a strong acid. Its sodium salt crystallises from water or alcohol in slender needles or transparent prisms, which become opaque in a dry atmosphere; a solution of the salt gives a brownish-yellow, crystalline precipitate with cupric salts. The silver salt is white, and crystallises from boiling water in microscopic prisms.

These results confirm the author's conclusion (Abstr., 1882, 1189) that the introduction of cyanogen into a CH_2 group which is already united to two other negative radicles results in the production of an acid function. The alkyl dicyanacetates may be regarded as alkyl cyanomalonates in which a group COOR has been displaced by CN.

C. H. B.

New Acid of the Acetic Series. By E. Gérard (*Compt. rend.*, **111**, 305—307).—The seeds of *Datura stramonium* are extracted with ether, the ether distilled off, and the residue purified by solution in light petroleum, filtration, and distillation. A greenish-yellow oil is thus obtained in quantity amounting to about 25 per cent. of the weight of the seeds. It is saponified by lead oxide, and the dried lead salts are treated with ether to remove lead oleate and linoleate, which are present

in considerable quantity. The residue is decomposed by hydrochloric acid, and the mixture of acids is dissolved in alcohol of 85°, the crystals which separate being purified by recrystallisation. Finally, the solution of the acid is fractionally precipitated by barium hydroxide, and the acid separated from the barium salt by treatment with hydrochloric acid, and purified by crystallisation from alcohol. It forms slender needles which melt at 55°, is somewhat soluble in cold alcohol, very soluble in boiling alcohol, ether, and light petroleum. It has the composition $C_{17}H_{34}O_2$, and is intermediate between palmitic and stearic acids, which it closely resembles, but its melting point is much lower. The author proposes to call it *daturic acid*. It is monobasic; the barium salt is anhydrous and insoluble in water, but crystallises from alcohol in microscopic needles; the zinc salt is very similar; the magnesium salt is also similar, but is much more soluble in hot alcohol. The ethyl salt, obtained in the same way as ethyl stearate, crystallises from strong alcohol in slender needles which melt at 27° and at 25° solidify in large lamellæ. C. H. B.

Addition of Chlorine and of Halogen Acids to Oleïc Acid and Elaïdic Acid. By S. Piotrowski (*Ber.*, **23**, 2531—2533).—*Dichlorostearic acid*, $C_{18}H_{34}O_2Cl_2$ is obtained when the theoretical quantity of chlorine is passed into a chloroform solution of elaïdic acid; it crystallises from alcohol in nacreous plates, melts at 32°, and is very readily soluble in all ordinary solvents except water. The *calcium* salt $(C_{18}H_{33}O_2Cl_2)_2Ca$ crystallises from hot absolute alcohol in needles, and is soluble in cold ether, but insoluble in cold alcohol; the *barium* salt has the same properties. The *methyl* salt, $C_{18}H_{33}Cl_2O_2Me$, crystallises in needles.

Chlorostearic acid, $C_{18}H_{35}O_2Cl$, can be prepared by saturating a glacial acetic acid solution of oleïc or elaïdic acid with hydrogen chloride at 0°, and keeping the solution for three to four days at the ordinary temperature. It crystallises from hot alcohol in slender needles, melts at 38°, and is readily soluble in most ordinary solvents except water. The *barium* salt is soluble in ether, but is precipitated from the solution on the addition of cold alcohol; the *calcium* salt shows a like behaviour.

Bromostearic acid, $C_{18}H_{35}O_2Br$, prepared in like manner from oleïc or elaïdic acid, melts at 41°, and resembles the corresponding chlorine derivative in its behaviour with solvents. F. S. K.

Lithium Malonates. By G. Massol (*Compt. rend.*, **111**, 233—234). —Heats of formation: $C_3H_4O_4$ + LiOH develops +12·66 Cal., $C_3H_3O_4Li$ + LiOH develops +12·87 Cal., $C_3H_4O_4$ + 2LiOH develops +25·53 Cal.

Lithium hydrogen malonate forms anhydrous, colourless, crystalline crusts readily soluble in water; heat of dissolution, −1·43 Cal.

Lithium malonate forms hard, white, anhydrous, crystalline masses; heat of dissolution, +3·54 Cal. The heat of formation of the solid salt from solid acid and base is +33·56 Cal. The following table gives the heats of formation of the solid alkaline malonates:—

	Potassium.	Sodium.	Ammonium.	Lithium.
Hydrogen salt..	+27·87 Cal.	25·86 Cal.	22·78 Cal.	17·63 Cal.
Normal salt....	+48·56 „	41·50 „	41·00 „	33·56 „

C. H. B.

Silver Malonate. By G. MASSOL (*Compt. rend.*, **111**, 234—235).—Silver malonate, obtained by double decomposition, is an anhydrous, slightly yellowish-white, crystalline powder consisting of slender, microscopic needles in stellate groups. It blackens when exposed to light, and when heated, burns with vivid deflagration, leaving a residue of metallic silver. It is only slightly soluble in water; heat of dissolution at 20°, −9·8 Cal. The heat of formation of the precipitated salt from dissolved silver nitrate and potassium malonate is +9·83 Cal., from the dissolved acid and precipitated silver oxide, +18·84 Cal. These numbers are lower than the corresponding values for silver oxalate. C. H. B.

Conversion of Maleïc Acid into Fumaric Acid. By Z. H. SKRAUP (*Monatsh.*, 11, 323—325).—Other acids besides the halogen acids and nitric can convert maleïc into fumaric acid; their action is proportional to their acid-strength. The electrical conductivity has a distinct influence, though not in any simple proportion, on the rate of change; in this respect, strong hydrochloric, nitric, and sulphuric acids act unequally. The presence of lithium and ammonium chlorides accelerates the action of hydrochloric acid.

Parabromobenzyl maleate is not changed when heated for some hours at 200°, or with alcohol at 150°, unless the latter contains iodine or acetic acid. Silver maleate and parabromobenzyl bromide yield parabromobenzyl maleate (m. p. 80°) only, when heated in ether at its boiling point; but at 150°, a small quantity of parabromobenzyl fumarate (m. p. 115°) is also formed.

In absence of water, parabromobenzyl maleate is changed into fumarate at the ordinary temperature by hydrochloric acid, and at higher temperatures by nitric acid and sulphuric acid, the last acting less readily than nitric acid.

It is pointed out that malic acid may be an intermediate product in the change of maleïc into fumaric acid. The subject is being further investigated. A. G. B.

Symmetrical Trimethylenetricarboxylic Acid. By E. BUCHNER and H. WITTER (*Ber.*, **23**, 2583—2585).—The further investigation of the acid (m. p. 220°) which is obtained from the additive product of ethyl fumarate and ethyl diazoacetate (compare Abstr., 1888, 1274) has shown that it is, as was supposed, symmetrical trimethylenetricarboxylic acid. It is not reduced by sodium amalgam even on boiling, and it is unchanged by concentrated hydrobromic acid, both in the cold and at 100°; as cis-1 : 2-trimethylenedicarboxylic acid, prepared by Conrad and Guthzeit's method, is also unchanged by concentrated hydrobromic acid at the ordinary temperature, the readiness with which 1 : 1-trimethylenedicarboxylic acid is decomposed by hydrobromic acid cannot be looked on as a general property of polycarboxy-derivatives of trimethylene.

The acid described as propargylenetetracarboxylic acid by Schacherl (Abstr., 1885, 1125) is 1 : 1 : 2 : 3-trimethylenetetracarboxylic acid. *Methyl trimethylenetetracarboxylate*, $C_3H_2(COOMe)_4$, is obtained when methyl bromofumarate is treated with ethyl sodiomalonate; it separates from ether in compact crystals, melts at 85°, boils at 205—215° under a pressure of 15 mm., and on hydrolysis it gives Schacherl's propargylenetetracarboxylic acid. The last-named compound is not acted on by potassium permanganate in alkaline solution, and when heated quickly to 196—198°, it is converted into trimethylenetricarboxylic acid (m. p. 220°) with evolution of carbonic anhydride.

F. S. K.

Acids of the Sugar Group. By E. Fischer (*Ber.*, **23**, 2625—2628).—d-Glucolactone is obtained in crystals when an aqueous solution of pure gluconic acid, prepared by decomposing the calcium salt with oxalic acid, is evaporated to a syrup, and then kept over sulphuric acid for 8—14 days; it can be purified by repeated recrystallisation from warm water, but it still shows a slight acid reaction. It melts at about 130—135°, has a sweet taste, and is very readily soluble in hot alcohol; its specific rotatory power is $[\alpha]_D = 68\cdot2$, but in the course of 24 hours the rotatory power gradually diminishes owing to partial conversion into the acid.

Gluconic acid seems to be very feebly levo-rotatory, but the solution quickly becomes dextro-rotatory, owing probably to the formation of lactone; a like behaviour is also exhibited by d-mannonic acid, as has been previously shown. On the other hand, the rotatory power of solutions of many lactones of this group gradually changes as they are partially converted into the acids, and it would seem that the so-called bi-rotation of the saccharoses is due to a similar cause; in aqueous solution, they are gradually converted into hydrated compounds which possess a rotatory power different from that of the anhydrous compound. All observations seem to show that anhydrous grape-sugar, for example, dissolves in water as the compound $C_6H_{12}O_6$, which is then gradually transformed into the heptahydric alcohol, $C_6H_{14}O_7$, the rotatory power becoming constant only when the change is complete.

Calcium l-mannonate, $(C_6H_{11}O_7)_2Ca + 3H_2O$, can be obtained in crystals by boiling an aqueous solution of pure l-mannolactone for half-an-hour with pure calcium carbonate, evaporating the filtered solution to a small volume, and adding alcohol to the hot solution in such quantities that it remains clear; the syrupy calcium salt which separates on cooling slowly solidifies when rubbed with a glass rod, and a crystal, introduced into a concentrated aqueous solution of the salt, causes the crystallisation of the whole. It forms slender needles, loses its water at 100°, and is readily soluble in warm, but only moderately easily in cold, water.

Arabonic acid phenylhydrazide, $C_5H_9O_5\cdot N_2H_2Ph$, is precipitated in yellowish crystals when a moderately concentrated solution of the acid, lactone, or calcium salt is heated with phenylhydrazine and 50 per cent. acetic acid for $1\frac{1}{2}$ hours at 100°. It crystallises from hot water in colourless plates, and melts at 215° with decomposition when quickly heated.

Xylosecarboxylic acid can be prepared by treating xylose with hydrocyanic acid in the usual manner. The basic *barium* salt crystallises from hot water, is very sparingly soluble in cold water, and has the composition $C_6H_{11}O_7Ba\cdot OH$; on decomposing the barium salt with the theoretical quantity of sulphuric acid and evaporating the solution, there remains a colourless syrup which consists of a mixture of acid and lactone. By reducing this mixture with sodium amalgam, a sugar is formed, the osazone of which is moderately easily soluble in hot water, and differs from all known hexosazones. F. S. K.

Hydroxygluconic Acid. By L. Boutroux (*Compt. rend.*, **111**, 185—187).—The author considers that the acid resembling glycuronic acid obtained by E. Fischer by the reduction of saccharic acid (this vol., p. 599) is probably identical with the hydroxygluconic acid which he obtained (Abstr., 1886, 682) by the action of a bacterium on glucose.

Hydroxygluconic acid, $C_6H_{10}O_7$, is lævogyrate, its rotatory power in a 2 per cent. solution being $[\alpha]_D = -14\cdot5^\circ$. Its lead salt forms small, yellowish-white, irregular crystals which are only slightly soluble in water. Lead acetate, however, does not always precipitate solutions of hydroxygluconates, because the lead salt has a great tendency to remain in supersaturation. Hydroxygluconic acid resembles glycuronic acid in many respects, although the former is lævogyrate and very soluble in alcohol, whilst the latter is dextrogyrate and insoluble in alcohol. C. H. B.

Conversion of Thiocarbamide into Carbamide. By R. Maly (*Monatsh.*, **11**, 277—281).—This conversion has not been directly effected hitherto. The author finds that the sulphur in thiocarbamide is directly oxidised to sulphuric acid by potassium permanganate in neutral solution, according to the equation $CH_4N_2S + O_4 = CH_4N_2O + SO_3$; the quantity of oxygen actually used falls a little short of four atoms, but this is to be accounted for by the fact that a small quantity of the sulphur makes its appearance as potassium thiosulphate.

In acid solution, the above reaction does not take place, a new base being formed under these circumstances. A. G. B.

Ammoniacal Fermentation of Uric Acid. By F. Sestini and L. Sestini (*Landw. Versuchs-Stat.*, **38**, 157—164).—Uric acid, suspended in water, may be kept for more than a year without undergoing any change, but the addition of a very small amount of decomposed urine causes it to decompose quickly and completely in hot weather. Pure uric acid (4 or 6 grams) was put into a large flask with distilled water (4 or 6 litres) and urine (1 or 2 c.c.) added. By means of a suction pump, 2 litres of air was made to pass through the liquid four or five times a day. In another experiment, a stoppered flask was employed; this was frequently shaken and opened. In a few days the liquid became alkaline from the formation of ammonium carbonate, and the amount of suspended uric acid diminished until, in seven or eight days, it disappeared entirely. In 12 or 13 days, the whole of the uric

acid was changed into ammonium carbonate. The reaction is expressed thus: $C_5H_4N_4O_3 + 8H_2O + 3O = 4NH_4HCO_3 + CO_2$. In another experiment, made at a temperature of 20°, the uric acid was almost all decomposed in 20 days, when the experiment was stopped. It was found that only a little more than half the total nitrogen was present as ammonia, the rest being in organic compounds.

In a third experiment, with a temperature of 22—28°, nearly all the uric acid disappeared within seven days. On the eighth day, a part of the liquid was taken out, filtered, and distilled. The result showed that about $\frac{12}{17}$ of the uric acid was converted into ammonium carbonate and the rest into carbamide. Another portion of the liquid, not filtered, was kept for eight days longer, when it was found that the whole of the uric acid was converted into ammonia. It is possible that further investigation may show that other componnds besides carbamide (alloxan, for instance) are formed as intermediate products. N. H. J. M.

Presence of Furfuraldehyde in Commercial Alcohols. By L. LINDET (*Compt. rend.*, **111**, 236—237).—The author has applied the aniline acetate test to a large number of commercial alcohols, and finds that, contrary to the usual statement, furfuraldehyde is not a constant constituent. If the alcohol has been distilled over a naked fire, or if it is derived from grain which has been in contact with acids, then it contains furfuraldehyde; but if distilled with steam, and the grain has not been in contact with acids, the alcohol is free from furfuraldehyde.

The following quantities of furfuraldehyde per litre of alcohol were found in various brandies: cognac, 0·2 c.c.; cider, 0·03 c.c.; cherry, 0·02 to 0·13 c.c.; marc, 0·1 to 0·4 c.c.; and it is doubtless produced by the partial destructive distillation of the vegetable matter held in suspension in the liquids.

Alcohol from sugar, obtained by the action of mineral acids, contains 0·06—0·1 c.c. of the aldehyde per litre, even when distilled with steam; before fermentation, in fact, the aldehyde can be detected in the wort. Pure maize starch, saccharified by acids, yields, however, only traces of furfuraldehyde. Worts fermented by diastase contain only very small quantities of the aldehyde, and its formation is probably due to the action of lactic acid. In the case of beer, the wort remains neutral, and no furfuraldehyde can be detected. Molasses brandy contains 0·04 to 0·05 c.c. of the aldehyde per litre of alcohol, not formed, as direct experiments show, by the action of acids on cane-sugar, but due to the addition, in place of yeast, of worts in full fermentation, these worts having been prepared from grain which has been in contact with acids.

Alcohol from beet, artichokes, and potatoes, fermented in absence of acids, and distilled by steam, contains no furfuraldehyde.

C. H. B.

Preparation of Thiophen. By L. H. FRIEDBURG (*Chem. Centr.*, 1890, ii, 8; from *J. Amer. Chem. Soc.*, **12**, 83—90).—By heating a mixture of sodium succinate and phosphorus trisulphide, the author

has obtained as much as 50 per cent. of the theoretical quantity of thiophen. He recommends that not more than 155 grams of sodium succinate, with twice the weight of phosphorus trisulphide, shall be employed in one operation. J. W. L.

Alteration of Compounds of the Benzene Series when Exposed to Air and Light. By A. BIDET (*Compt. rend.*, 111, 47; compare Abstr., 1889, 595).—Many compounds, including aniline chloride, sulphate, and nitrate, toluidine, resorcinol, benzoic chloride, benzaldehyde, nitrocinnamic acids, naphthol, naphthylamine, and quinoline and its salts, were carefully purified, and remained quite colourless even after exposure to air and light for several months. The purest obtainable commercial samples of the same compounds became decidedly coloured when exposed under the same conditions, though they remained colourless if kept in the dark. From these results and his previous observations (*loc. cit.*), the author concludes that the property of becoming coloured when exposed to air and light is not inherent in pure organic compounds, but is due to the presence of impurities, the proportion of which, in some cases, may be very small indeed. C. H. B.

Action of Nitrons Anhydride on Various Substances in Solution in Carbon Bisulphide. By L. H. FRIEDBURG and J. A. MANDEL (*Chem. Centr.*, 1890, ii, 8—9; from *J. Amer. Chem. Soc.*, 12, 7—12).—The nitrous anhydride, prepared by heating arsenious anhydride with nitric acid, was purified by passing it over lead and collected in a cooled receiver. It was afterwards mixed with carbon bisulphide and added drop by drop to the several substances, also dissolved in carbon bisulphide. With benzene, mononitro- and para-dinitro-benzene are formed; with phenol, ortho- and para-nitrophenols and nitrosophenols are formed; with diphenylamine, para-nitro-diphenylamine and ortho- and para-dinitro-diphenylamine are formed, together with undefined nitroso-compounds. Attempts to introduce sulphur into the diphenyl molecule at the same time, by dissolving it in the carbon bisulphide, were unsuccessful. With diphenyl, nitrous anhydride reacts, with formation of paranitrodiphenyl, and another substance not yet investigated. Nitrous anhydride does not react with benzonitrile under ordinary pressures; it oxidises benzaldehyde to benzoic acid. With benzoic acid, it forms *nitrosobenzoic acid*, melting at 114°. Its barium salt, $(C_6H_4NO{\cdot}COO)_2Ba$, crystallises with 2 mols. H_2O. J. W. L.

Artificial Musk. By A. BAUR (*Compt. rend.*, 111, 238—240).—Metaisobutyltoluene is heated on a water-bath for 24 hours with five times its weight of a mixture of sulphuric acid and fuming nitric acid. The product is subjected to a repetition of the same treatment, and is thus completely converted into trinitrobutyltoluene, which crystallises from alcohol in white needles melting at 96—97°, and insoluble in water, but soluble in alcohol, ether, and the usual solvents. Even in very dilute solutions this compound has a strong odour of musk, and for many purposes may replace the natural

product. The latter, however, is quite different in composition; it is a non-nitrogenous resin. Trinitrobutyltoluene has no poisonous effects. It combines with naphthalene (in the proportion of 2 mols. of trinitrobutyltoluene to 1 of naphthalene), forming a compound which crystallises from alcohol in large, white lamellæ melting at 89—90°; when distilled with water, naphthalene passes over, and the trinitro-derivative remains in the retort.

The homologues of isobutyltoluene behave in a similar manner. Trinitroisobutylmetaxylene, which forms white needles melting at 110°, has an odour which cannot be distinguished from that of trinitroisobutyltoluene. C. H. B.

Action of Iodide of Nitrogen on some Organic Compounds. By R. LEPETIT (*Gazzetta*, **20**, 104—108).—When moist iodide of nitrogen is agitated with a cold aqueous solution of phenol containing a few drops of caustic soda, a deep-blue solution and a greyish precipitate are formed, with copious evolution of ammonia. The solution contains a mixture of mono-, di-, and tri-iodophenols, the blue coloration being probably due to a small quantity of some azotised product. The precipitate, which is probably identical with Lautemann's triiodophenol, crystallises from dilute alcohol in colourless needles, melts at 155°, dissolves in caustic potash and soda forming blue solutions, and is decomposed by concentrated nitric and sulphuric acids with separation of iodine.

α- and β-naphthol are differently affected by iodide of nitrogen; on adding an alkaline solution of β-naphthol to the strongly cooled iodide, a brownish-green precipitate is formed, which redissolves after standing for some time. From the solution, a current of sulphurous anhydride precipitates a moniodonaphthol which melts at 94·5°, and is otherwise identical with Meldola's orthiodonaphthol. When iodide of nitrogen is added to β-naphthol, only a slight deposit of dinaphthol is formed.

On adding a solution of α-naphthol in caustic soda to moist iodide of nitrogen, or *vice versâ*, a light, violet-black precipitate is formed which greatly resembles the iodide in appearance, but does not evolve iodine on heating or on treatment with strong acids. It is insoluble in alcohol, acetic acid, ether, chloroform, alkalis, and acids, but dissolves in aniline; on heating, it partially fuses and decomposes, leaving a carbonaceous residue.

With iodide of nitrogen, salicylic acid forms a reddish, amorphous, unstable compound which decomposes with separation of iodine. Acetone yields iodoform and a substance having the pungent odour of an iodacetone. With ethyl acetoacetate, a yellowish oil is obtained; diazobenzene chloride is decomposed on addition of iodide of nitrogen into benzene and resinous products. S. B. A. A.

Reduction Products of Iodophenols. By J. MESSINGER and N. PICKERSGILL (*Ber.*, **23**, 2761—2764).—Iodothymol is dissolved in ether, alcoholic potash added, and then zinc-dust in successive small quantities, the mixture being finally boiled for two days in a reflux apparatus. The alcohol is evaporated as far as possible,

water being continually added, and then, on the addition of dilute sulphuric acid, a substance is precipitated which, after careful purification, crystallises from dilute acetic acid or alcohol in small, white needles melting at 160°. It is *dithymol*,

$$OH{\cdot}C_6H_2MePr^{\alpha}{\cdot}C_6H_2MePr^{\alpha}{\cdot}OH + 2H_2O,$$

probably [Me : OH : Pr^{α} : $C_{10}H_{13}O$ = 1 : 3 : 4 : 6], since it gives no nitroso-derivative with nitrous acid, as compounds usually do in which the hydrogen that stands in the para-position to the hydroxyl is not replaced. The *benzoyl* derivative, prepared from dithymol and benzoic chloride, crystallises from benzene in thick, white tables which melt at 209—210°, and dissolve easily in benzene and chloroform, sparingly in alcohol, ether, and light petroleum. The *acetyl* derivative, prepared from dithymol and acetic anhydride, crystallises from alcohol in needles which melt at 113—114°, and dissolve easily in alcohol, ether, benzene, light petroleum, and chloroform.

C. F. B.

Action of Hydroxylamine on Nitrosophenols. By F. KEHRMANN and J. MESSINGER (*Ber.*, **23**, 2815—2820).—β-Naphthaquinonedioxime is prepared by the action of hydroxylamine (2—3 mols.) on nitroso-β-naphthol dissolved in excess of aqueous soda; the reaction proceeds in the cold, and the dihydroxime is precipitated on the addition of dilute sulphuric acid; it melts at 180—181°, and its preparation in this manner affords a ready means of obtaining 1 : 2-naphthylenediamine.

Diquinoyltetroxime is formed in a similar manner from dinitrosoresorcinol. On treating with 5 parts of nitric acid of sp. gr. 1·45, diluting with ice water, and adding potassium carbonate, a potassium salt is deposited which crystallises from water in brownish-yellow needles, and is being further investigated. A corresponding compound is obtained from toluenetetroxime, prepared from dinitroso-orcinol and hydroxylamine. Attempts to obtain benzene hexoxime were unsuccessful.

On treating paranitrosophenol with hydroxylamine as above, and extracting the acid solution with ether, white crystals are obtained which quickly decompose, with the formation of phenol and a considerable quantity of resinous matter. Nitrosothymol behaves in a similar manner; on dissolving the white compound in aqueous soda and adding an equal weight of some phenol, such as cresol, thymol, phenol, or α-naphthol, but not β-naphthol, an intense blue colour is produced, which turns red on the addition of an acid, and, after some time, becomes colourless. The blue compound could not be obtained in crystals. Bromonitrothymol behaves in a similar manner. The above reactions may be explained by assuming that paraquinoneoxime reacts with hydroxylamine as if it were a trinitrosophenol, and yields diazophenol; by the further action of hydroxylamine, hydrogen diazophenol, $OH{\cdot}C_6H_4{\cdot}NH{\cdot}NH{\cdot}OH$ (the white compound), is formed, and this then decomposes into phenol, nitrogen, and water.

J. B. T.

Desmotropy in Phenols. By J. HERZIG and S. ZEISEL (*Monatsh.*, 291—310, 311—322; compare Abstr., 1888, 822; 1889, 247, 966).—For the ethylation of resorcinol, the latter (100 grams) is dissolved in absolute alcohol (1 litre), potassium hydroxide (204 grams) is added, and the mixture is warmed until everything has dissolved; ethyl iodide (567 grams) is then slowly added, and the warming continued until the liquid is neutral, when more potassium hydroxide and ethyl iodide are added, and the heating continued until the liquid is once more neutral. The alcohol is now distilled off, and the oil precipitated with water and shaken with ether; the ethereal solution is washed successively with alcoholic potash and water, and distilled. The dried residue amounted to 154 per cent. of the resorcinol; it was first fractionally distilled at 40 mm. pressure.

The first two fractions boiled, under the ordinary pressure, at 228—232°, and consisted largely of resorcinol diethyl ether; the other portion was not investigated. Resorcinol diethyl ether, $C_6H_4(OEt)_2$, crystallises in transparent, colourless prisms which melt at 12·4°: it boils, at 0° and 756 mm., at 234·4—235·2° (corr.; Barth, 235—236°; Pukall, 228—230°); it has a characteristic odour, and gives a green colour with acetic acid and potassium nitrite.

Two isomeric bromo-derivatives are obtained by brominating resorcinol diethyl ether in glacial acetic acid (20 parts), precipitating with water, and crystallising from alcohol; they are separated by carefully adding water to their solution in acetic acid, as long as the crystals that separate vary in melting point. In this way, *α-dibromoresorcinol diethyl ether* is obtained first; it crystallises in long, slender, colourless prisms which melt at 100—101°. *β-Dibromoresorcinol diethyl ether* crystallises in colourless needles, and melts at 75—77°.

The remaining fractions were again fractionated at 19 mm.; the two chief products thus obtained boiled at 146—151° and 160—165° respectively. The former of these is a dark resin, insoluble in water, but soluble in alkalis to a red liquid with a green fluorescence; its analysis gives numbers which agree, as far as carbon and hydrogen are concerned, with ethylresorcinol diethyl ether, $C_6H_3Et(OEt)_2$, but the numbers for ethoxyl do not agree with this formula. It is probable that other triethyl-derivatives of resorcinol are also present.

The fraction boiling at 160—165° consists of *secondary-tertiary-triethylresorcinol ethyl ether*, $C_6H_2Et_3O{\cdot}OEt$; it forms a thick, yellow oil with a somewhat spicy odour; it dissolves in strong sulphuric acid with an intense yellow colour, and is precipitated unchanged by water. It is soluble in most organic solvents.

Secondary-tertiary-triethylresorcinol, $C_6H_2Et_3O{\cdot}OH$, is obtained (9 per cent.) when the above ethyl ether is heated with 20 per cent. hydrochloric acid in a reflux apparatus for two hours; the reaction product is shaken with dilute potash solution, and the solution acidified and shaken with ether. When recrystallised from alcohol, it forms white needles, melts at 183—185°, and is soluble in alcohol, light petroleum, and ether. The *acetyl derivative*, $C_6H_2Et_3O{\cdot}OAc$, forms monosymmetric crystals ($a : b : c = 0{\cdot}7089 : 1 : 1{\cdot}0243$; $\beta = 65° 16' 24''$) melting at 63—65°.

The authors doubt the existence of De Luynes' and Lionet's "triethylorcinol" (*Compt. rend.*, 65, 213). Pelizzari has privately informed them of the results of a research in which he has obtained a substance agreeing in analysis with the formula $C_7H_5Et_2O{\cdot}OEt$, and thus apparently established De Luyne's and Lionet's compound; the authors, however, have failed to obtain it.

The ethylation of orcinol is conducted similarly to that of resorcinol (see above). The product was fractionally distilled at 20 mm. pressure, and the following definite compounds have been isolated:—

Orcinol diethyl ether, $C_7H_6(OEt)_2$, constitutes the fraction distilling at 144—150° (20 mm.), and is obtained pure by fractionally freezing the crude product until a portion melting at 16—16·5° is obtained. It crystallises in white needles, boils at 250·9—251·9° (corr., 0° and 745 mm.), and is insoluble in water, but dissolves in the usual organic solvents. *Dibromorcinol diethyl ether*, forms long, white needles; it melts at 142—144°, and dissolves sparingly in cold glacial acetic acid and cold alcohol, but more freely in hot alcohol.

The fraction boiling at 165—170° (20 mm.) is probably a mixture of $C_7H_4Et_3O{\cdot}OEt$ and $C_7H_4Et_2(OEt)_2$, but neither of them has been isolated from this fraction.

Secondary-tertiary-triethylorcinol ethyl ether, $C_7H_4Et_3O{\cdot}OEt$, constitutes the fraction which boils at 175—180°; its properties are not described in the paper.

Secondary-tertiary-triethylorcinol, $C_7H_4Et_3O{\cdot}OH$, is obtained when the above ethyl ether is heated with hydrochloric acid (sp. gr. 1·1) for three hours in a reflux apparatus. The product is dissolved in ether and the solution shaken with dilute potash; the potash solution is then acidified and shaken with ether, which dissolves the new compound. When recrystallised from alcohol, it forms colourless needles which melt at 142—144°, and are insoluble in water. The *acetyl derivative*, $C_7H_4Et_3O{\cdot}OAc$, forms colourless, monosymmetric crystals ($a : b : c = 0{\cdot}6369 : 1 : ?$; $\beta = 60°\ 8'\ 37''$) which melt at 71—73°. By saponifying the acetyl-derivative with sodium hydroxide, it is reconverted into the original triethylorcinol melting at 192—193°. [The authors apparently ignore the fact that they have already given the melting point as 142—144°.—ABSTRACTOR.]

A. G. B.

Orceïn. By K. ZULKOWSKI and K. PETERS (*Monatsh.*, 11, 227—245).—The authors have obtained three distinct colouring matters by the action of ammonia and air on orcinol, and find that the formulæ hitherto given for orceïn are based upon analyses of impure products.

50 grams of crystallised orcinol are dissolved in water (200 c.c.), and ordinary ammonia solution (200 c.c.) is added. The mixture is put into a large flask and covered with a beaker. After some two months, the liquid becomes a thickish magma; this is transferred to a thick-walled flask, warmed on the water-bath, and the ammonia removed, as far as possible, by means of a water-pump. Hydrochloric acid is then added until the liquid is neutral, and the resulting precipitate, which contains all three colouring matters, is filtered, washed with water, and dried at as low a temperature as possible.

What colouring-matter remains in the filtrate is thrown out, after concentration, by sodium chloride, and dried. The mixed precipitates are washed with ether for eight days, to dissolve the yellow colouring-matter, and then with water to remove salt, and, finally, heated with strong alcohol for some time and filtered while hot, whereby the orceïn is dissolved and the third colouring-matter left undissolved. To obtain the orceïn, the alcoholic solution is evaporated, diluted with water, again heated, and allowed to cool slowly, when the orceïn crystallises; it is filtered off and dried in a vacuum.

Thus prepared, orceïn, $C_{28}H_{24}N_2O_7$, is a brown powder, and only shows a metallic lustre when dried in masses; under the microscope it is found to consist of very small, felted crystals. It is insoluble in water, ether, benzene, chloroform, and carbon bisulphide, but dissolves in acetone, glacial acetic acid, and alcohol; the solution is carmine, and becomes bluish-violet on addition of alkalis. Strong sulphuric acid dissolves orceïn in the cold to a bluish-violet solution, which is not precipitated, but is turned carmine by water.

To obtain the *yellow* colouring-matter, $C_{21}H_{19}NO_5$, the ethereal solution (see above) is distilled, and the residue (about 15 per cent. of the original orcinol) dissolved in hot alcohol and filtered; the filtrate is diluted with water, warmed until the precipitated colouring-matter has redissolved, and left to crystallise. When dry, it is a brown powder, which has a green metallic lustre, and consists of well formed, deep-yellow microscopic prisms; it is slightly soluble in hot water, freely so in ether and in alcohol, to an orange-yellow solution, which is changed to deep-violet by alkalis. Strong sulphuric acid dissolves it to a violet solution.

The third colouring-matter, left undissolved by the alcohol, is an amorphous powder, which is insoluble in all the usual solvents, and hence can not be purified for analysis. It has a green metallic lustre, and dissolves in ammonia and alkalis with a dark blue colour, which is turned onion-red when the solution is diluted and acidified; it separates from the acid solution, after a time, in cherry-red flocks. This substance is possibly identical with litmus, and is being further investigated.

No orceïn was obtained by the action of air on an alkaline solution of orcinol.

Orceïn can be more quickly prepared by acting on orcinol (100 parts) with ammonia (6 parts) and hydrogen dioxide (35 parts); the two bye-products described above are formed in this case also, and the separation is carried out in the same way.

A colouring-matter is obtained by acting on resorcinol with ammonia and hydrogen dioxide; it dissolves in alcohol to a dirty-red solution, but not in other solvents; it resembles the litmus-like substance described above, but has not been further investigated.

When a mixture of orcinol (142 parts) and resorcinol (110 parts) is acted on by hydrogen dioxide (3400 parts of 3 per cent. solution) in ammonia (7·7 parts of 22 per cent. solution) for some days, and the solution acidified, a precipitate is obtained which yields a magenta-red solution when digested with alcohol, and an insoluble colouring-matter (18 per cent.) similar in properties to litmus. The

alcoholic solution contains a new colouring matter, *reso-orcein*, $C_{28}H_{20}N_2O_7$; this, by diluting with water and crystallising the solution, is obtained in fragments, having a lustre like bronze, and consisting of microscopic crystals. Reso-orcein differs from orceïn in being more soluble in dilute alcohol, and in the solution having a bluer shade and becoming a pure blue when alkaline; moreover, it dissolves with a brilliant blue colour in strong sulphuric acid. Further experiments were tried to obtain colouring matters from mixtures of orcinol and higher phenols, but with indefinite results. The whole subject is still under investigation. A. G. B.

Tetramethylphloroglucinol. By A. SPITZER (*Monatsh.*, **11**, 287—290).—When tetramethylphloroglucinol (1 gram; this vol., p. 1110), is heated with 40 per cent. hydrochloric acid (20 c.c.) in a sealed tube at 200° for seven hours, acetic, isobutyric, and carbonic acids, diisopropyl ketone, and, perhaps, methyl isopropyl ketone are obtained. A. G. B.

Reduction of Nitriles. By M. FREUND and P. IMMERWAHR (*Ber.*, **23**, 2845—2858).—Diphenylacetonitrile is dissolved in alcohol and treated with 2·5 times the theoretical quantity of sodium, the product is distilled in a current of steam, the distillate neutralised with hydrochloric acid and extracted with ether; on evaporation, diphenylmethane is obtained. The aqueous solution is evaporated, and the residue recrystallised from alcohol; white needles are deposited on cooling, which melt at 255°, and consist of asymmetrical *β-diphenylethylamine hydrochloride*, $CHPh_2·CH_2·NH_2,HCl$. It may also be obtained in the form of rhombic plates. The *platinochloride* forms a pale yellow, crystalline powder. The *free base* is a colourless, viscid liquid.

Benzylfurfuryl, $C_4OH_3·CH_2·CH_2Ph$, is prepared in a similar manner by the reduction of α-phenylfurfuracrylonitrile, $C_4OH_3·CH{:}CPh·CN$; it is a colourless, oily liquid boiling at 241°, and is readily miscible with alcohol, ether, benzene, and carbon bisulphide; the yield is 30—40 per cent. of the nitrile employed. All attempts to prepare hydrogen, bromine, and nitro-derivatives were fruitless, nor could the furfuran ring be eliminated by the action of hydrochloric acid.

γ-Furfur-β-phenylpropylamine (β-furfurylphenylethylamine),

$$C_4OH_3·CH_2·CHPh·CH_2·NH_2,$$

is obtained, together with the previous compound, as a colourless, oily liquid boiling at 282—283°; it is miscible with alcohol and ether. The *hydrochloride* is prepared by adding concentrated hydrochloric acid to the free base; it is readily soluble in water, and melts at 176°. The *platinochloride* forms a pale yellow, crystalline powder, which commences to decompose at 150°, and melts at 175°. The *aurochloride* crystallises in pale yellow, metallic, lustrous needles, which readily decompose. The *mercurochloride* crystallises in white needles melting at 175°. The *picrate* is a light yellow, crystalline powder melting at 152°. *γ-Furfur-β-phenylpropylcarbamide*,

$$C_4OH_3·CH_2·CHPh·CH_2·NH·CO·NH_2,$$

is prepared by the action of potassium cyanate on the amine, and is deposited from absolute alcohol in lustrous crystals which melt at 101°. The corresponding phenylthiocarbamide,

$$C_4OH_3\cdot CH_2\cdot CHPh\cdot CH_2\cdot NH\cdot CS\cdot NHPh,$$

is formed by the action of phenylthiocarbamide, and is obtained from alcohol in white crystals melting at 113°. *γ-Furfur-β-phenylpropyl alcohol*, $C_4OH_3\cdot CH_2\cdot CHPh\cdot CH_2\cdot OH$, is a colourless liquid, and is prepared by the action of silver nitrite on the amine hydrochloride.

α-Paranitrophenylfurfuracrylonitrile, $C_4OH_3\cdot CH\colon C(CN)\cdot C_6H_4\cdot NO_2$, is formed by the action of a small quantity of sodium ethoxide on paranitrobenzyl cyanide and furfuraldehyde. It crystallises from alcohol in slender needles, and from benzene in nodular aggregates, melting at 171—173°. Attempts to reduce this compound were not very successful. On heating amidobenzyl cyanide and furfuraldehyde in molecular proportion, a compound with the formula $C_4OH_3\cdot CH\colon N\cdot C_6H_4\cdot CH_2\cdot CN$ is obtained, crystallising from alcohol in lustrous plates melting at 93—94°; on exposure to the air, it becomes red in colour. *α-Paramidophenylfurfuracrylonitrile*,

$$C_4OH_3\cdot CH\colon C(CN)\cdot C_6H_4\cdot NH_2,$$

is prepared by the action of sodium ethoxide on furfuraldehyde and amidobenzyl cyanide; it crystallises from alcohol in needles melting at 111—112°. The *diacetyl derivative*, $C_4OH_3\cdot CH\colon C(CN)\cdot C_6H_4\cdot NAc_2$, is obtained from diacetylamidobenzyl cyanide and furfuraldehyde in a similar manner, and is deposited from alcohol in pale yellow crystals which melt at 203—204°.

An *allylthiocarbamide*, with the formula

$$CN\cdot CH_2\cdot C_6H_4\cdot NH\cdot CS\cdot NH\cdot C_3H_5,$$

is formed by the action of allylthiocarbamide on amidobenzyl cyanide; on treating this compound with furfuraldehyde, an insoluble substance is obtained which melts at 206—208°, and has the formula

$$C_4OH_3\cdot CH\colon C(CN)\cdot C_6H_4\cdot NH\cdot CS\cdot NH\cdot C_3H_5.$$

Amidobenzylcyanophenylthiocarbamide melts at 140—141°; on treatment with furfuraldehyde, the compound

$$C_4OH_3\cdot CH\colon C(CN)\cdot C_6H_4\cdot NH\cdot CS\cdot NHPh$$

is formed; it may be crystallised from alcohol, and melts at 159—160°.

α-Phenyl-β-cinnamenylacrylonitrile, $CHPh\colon CH\cdot CH\colon CPh\cdot CN$, is prepared by the action of sodium ethoxide on cinnamaldehyde and benzyl cyanide; it crystallises from alcohol in slender needles melting at 118—119°, and is insoluble in water. By the reduction of this compound, an amine is formed in very small quantity, but the chief product is *diphenylbutylene*, $CHPh\colon CH\cdot CH_2\cdot CH_2Ph$, which is deposited from alcohol in white crystals melting at 39°; it readily dissolves in ether and chloroform, but is insoluble in water. The *dibromide*, $CHPhBr\cdot CHBr\cdot CH_2\cdot CH_2Ph$, is obtained by the action of bromine in the cold, and crystallises from alcohol in white needles

melting at 83°. By the action of fuming nitric acid on the hydrocarbon, a compound is formed which melts at 191°, and is probably a *tetranitro-derivative*. *Diphenylbutane*, $CH_2Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Ph$, is prepared by the reduction of the unsaturated compound with hydriodic acid and phosphorus at 250°; it is deposited from alcohol in white crystals which melt at 52°, and are insoluble in water, but readily dissolve in chloroform or ether. J. B. T.

Triphenylamine Derivatives. By R. HERZ (*Ber.*, **23**, 2536—2542; compare Heydrich, Abstr., 1886, 1105).—*Nitrotriphenylamine*, $NPh_2{\cdot}C_6H_4{\cdot}NO_2$, is formed when finely divided triphenylamine is gradually treated with nitric acid of sp. gr. 1·48 in glacial acetic acid solution, first at the ordinary temperature, and then at 45—50°. It crystallises from dilute acetic acid in golden plates, melts at 139—140° with decomposition, and is readily soluble in warm benzene, ether, glacial acetic acid, &c., but only sparingly in water and cold dilute alcohol. It dissolves in concentrated sulphuric acid yielding a dark blue solution, and, on reduction with tin and hydrochloric acid, it is converted into amidotriphenylamine, the *hydrochloride* of which crystallises in colourless, sparingly soluble needles, and has the composition $C_{18}H_{16}N_2,HCl$.

Amidotriphenylamine is a colourless, crystalline compound, which rapidly oxidises, and becomes reddish-violet on exposure to the air; its *acetyl* derivative, $NPh_2{\cdot}C_6H_4{\cdot}NHAc$, crystallises from dilute acetic acid in long needles melting at 197°.

Dinitrotriphenylamine, $NPh(C_6H_4{\cdot}NO_2)_2$, is obtained by nitrating triphenylamine as described above, but at a slightly higher temperature (55—60°). It crystallises from dilute acetic acid in slender, yellow needles, melts at 206—207°, and is readily soluble in benzene and boiling glacial acetic acid, but only sparingly in ether and hot alcohol, and insoluble in water and cold alcohol; it dissolves in concentrated sulphuric acid with a bluish-violet coloration.

Diamidotriphenylamine, $NPh(C_6H_4{\cdot}NH_2)_2$, prepared by reducing the dinitro-compound with tin and hydrochloric acid, crystallises from very dilute alcohol in colourless needles, and melts at 187° with decomposition. The *hydrochloride*, $C_{18}H_{17}N_3,2HCl$, crystallises in colourless plates, and is readily soluble in water. The *diacetyl* derivative, $C_{22}H_{21}N_3O_2$, crystallises from dilute acetic acid in colourless plates, and melts at 268—269°.

The author could not obtain the saffranine reaction with triamidotriphenylamine hydrochloride and chloranil under the conditions described by Heydrich (*loc. cit.*); the mono-, di-, and tri-amido-derivatives of triphenylamine all give deep blue or violet induline-like colour reactions when treated with chloranil in glacial acetic acid solution under various conditions. When, however, a very small quantity (about 0·0005 gram) of triamidotriphenylamine hydrochloride is dissolved in concentrated sulphuric acid (5 c.c.) containing a trace of fuming nitric acid, a dark-green solution is produced, which becomes deep blue on warming; on the gradual addition of water to the well-cooled solution, the colour changes to magenta-red, and a beautiful, red fluorescence is observed.

A compound of the composition $NHPh_2,2C_6H_2Cl(NO_2)_3$ is deposited in deep red needles when diphenylamine (1 mol.) is warmed with picryl chloride (2 mols.) in toluene solution, and the solvent partially evaporated; it melts at 65—66° with partial decomposition, is readily soluble in all ordinary solvents except water, and is decomposed by boiling dilute potash.

Triphenylaminetrisulphonic acid can be obtained by heating finely-divided triphenylamine with fuming sulphuric acid for a short time at 60°; the *sodium* salt, $N(C_6H_4{\cdot}SO_3Na)_3$, separates from alcohol as a crystalline powder, and is very readily soluble in water.

Diphenylnaphthylamine, $C_{10}H_7{\cdot}NPh_2$, prepared by treating potassiodiphenylamine with α-bromonaphthalene in boiling aniline solution, crystallises from boiling dilute alcohol in colourless needles, melts at 142°, boils at 335—340° (80—85 mm.), and is very readily soluble in most ordinary warm solvents, but almost insoluble in cold dilute alcohol, and insoluble in water; it dissolves in concentrated sulphuric acid yielding a light-green solution, and on warming, a sulphonic acid is formed. F. S. K.

Dinitrodimethylamidodiphenylamine. By E. LELLMANN and F. MACK (*Ber.*, **23**, 2739—2740).—If a concentrated aqueous solution of dinitrochlorobenzene [$Cl : (NO_2)_2 = 1 : 2 : 4$] (1 mol.), paramidodimethylamine hydrochloride (1 mol.), and soda (3 mols.) is warmed on the water-bath, *dinitrodimethylamidodiphenylamine*,

$$NMe_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_3(NO_2)_2,$$

separates; it crystallises in bronze-coloured scales melting at 168°. The *hydrochloride*, $C_{14}H_{14}N_4O_4,HCl$, forms yellow crystals, which are decomposed by water. When it is reduced with hydrochloric acid and zinc-dust, a colourless solution is finally obtained, doubtless containing the compound $NMe_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_6H_3(NH_2)_2$. If the neutral or slightly alkaline solution is allowed to remain in contact with air, a blue colouring matter separates out at the surface. C. F. B.

Xylylhydrazine. By A. KLAUBER (*Monatsh.*, **11**, 282—286).—*Sodium α-metaxylylhydrazinesulphonate* is prepared as follows:—50 grams of finely-powdered α-metaxylidine hydrochloride are suspended in a mixture of 200 grams of water and 40 grams of hydrochloric acid. The mixture is well cooled, and a concentrated solution of 25 grams of sodium nitrite is poured in; 250 grams of normal sodium sulphite is then added, and the whole well shaken, when it becomes at first red, and subsequently light yellow. The mixture is then warmed until the precipitate dissolves, and treated with zinc-dust and acetic acid until colourless, after which it is concentrated until the new salt crystallises. It forms colourless tables ($\frac{1}{2}$ mol. H_2O) which decompose at 250°, and are sparingly soluble in alcohol and water.

α-Metaxylylhydrazine, $C_8H_9N_2H_3$, is obtained as its *hydrochloride* when the above salt is decomposed by hydrochloric acid, and is prepared from this by adding an alkali; it crystallises in slender, pale-yellow needles which melt at 85°, and decompose when distilled, even in carbonic anhydride, with evolution of ammonia. It decomposes in

air forming oily substances and ammonia. It is sparingly soluble in water, more freely in ether, and very freely in alcohol. It reduces Fehling's solution on warming. In behaviour it is analogous to pheuylhydrazine. A. G. B.

Orthanisamine and Salicylamine. By H. GOLDSCHMIDT and H. W. ERNST (*Ber.*, **23**, 2740—2746).—*Orthanisaldoxime*,

$$OMe{\cdot}C_6H_4{\cdot}CH{:}NOH,$$

was obtained by warming orthanisaldehyde with a neutral solution of hydroxylamine. It crystallises from alcohol in long, white needles melting at 92°. *Carbanilido-orthanisaldoxime*,

$$OMe{\cdot}C_6H_4{\cdot}CH{:}NO{\cdot}CO{\cdot}NHPh,$$

is formed when equal molecular proportions of the oxime and phenyl cyanate are warmed together. It forms small, white needles melting at 105°, and is decomposed by alkalis.

Orthanisamine, $OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH_2$, is formed by reducing the oxime with sodium amalgam and acetic acid. It is a colourless liquid boiling at 224° under 724 mm. pressure. It dissolves in most solvents, and its aqueous solution is strongly alkaline. It readily absorbs carbonic anhydride from the air, solidifying to a white mass. The *hydrochloride*, $C_8H_{11}NO,HCl$, crystallises from alcohol in white prisms which melt at 150°, and are very soluble in water. The *platinochloride*, $(C_8H_{11}NO)_2,H_2PtCl_6 + 2H_2O$, crystallises from water in brilliant, golden-yellow plates melting at 187. *Orthanisylacetamide*, $OMe{\cdot}C_6H_4{\cdot}CH_4{\cdot}CH_2{\cdot}NHAc$, formed by the action of acetic acid on the amine, crystallises from alcohol in long, colourless needles which melt at 97°, and dissolve also in ether. *Orthanisylcarbamide*, $OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH_2$, formed by the action of potassium cyanate on the hydrochloride of the amine, crystallises from water in long, transparent needles melting at 127°. *Orthanisylphenylcarbamide*, $OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NHPh$, formed by the action of phenyl cyanate on the amine, crystallises from alcohol in long, colourless needles which melt at 145°, and dissolve also in ether and benzene.

Salicylamine or *orthohydroxybenzylamine*, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH_2$, was obtained by heating the hydrochloride of the amine for several hours with concentrated hydrochloric acid in sealed tubes at 150°. It crystallises from ether in groups of small needles which melt at 121°, have a smell resembling that of aldehyde-ammonia, dissolve in alkalis, and exhibit both basic and phenol-like properties. The *hydrochloride*, C_7H_9NO,HCl, crystallises from alcohol in colourless needles. The *platinochloride*, $(C_7H_9NO)_2,H_2PtCl_6 + 2H_2O$, crystallises from water in golden-yellow needles which melt with decomposition at 197°. *Orthohydroxybenzylacetamide*, $OH{\cdot}C_6H_4{\cdot}NHAc$, formed by the action of acetic anhydride on salicylamine, crystallises from ether in colourless needles melting at 140°. An attempt to prepare a diacetyl derivative was unsuccessful. *Orthohydroxybenzylcarbamide*, $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH_2$, obtained from salicylamine hydrochloride and potassium cyanate, crystallises from alcohol in colourless prisms melting at 170°, and soluble in hot water and alkalis. *Ortho-*

hydroxybenzylphenylcarbamide, $OH\cdot C_6H_4\cdot CH_2\cdot NH\cdot CO\cdot NHPh$, formed from salicylamine and phenyl cyanate, crystallises from alcohol in groups of small needles which melt at 155°, and dissolve also in ether, benzene, and alkalis. C. F. B.

Oximes. By H. GOLDSCHMIDT (*Ber.*, **23**, 2746—2749).—*Paraditolylketoxime*, $C_6H_4Me\cdot C(NOH)\cdot C_6H_4Me$ [$CNOH : Me : Me = 1 : 4 : 4'$], was prepared by acting on paraditolyl ketone (obtained from paratoluic chloride, toluene, and aluminium chloride) with an alkaline solution of hydroxylamine. It crystallises from alcohol in brilliant, transparent prisms which melt at 163°. When heated with concentrated sulphuric acid, it is transformed into an isomeric substance which crystallises from alcohol in colourless needles melting at 160°, and differing from the ketoxime in its insolubility in alkalis. It was shown to be the paratoluidide of paratoluic acid,

$$C_6H_4Me\cdot CO\cdot NH\cdot C_6H_4Me\ [CO : Me = 1 : 4,\ NH : Me = 1 : 4],$$

because when it is heated at 200° with concentrated hydrochloric acid in a sealed tube, paratoluic acid and paratoluidine are formed. It follows then that in the transformation of a ketoxime into a substituted acid amide, the nitrogen atom takes the place in the benzene ring that was previously occupied by the carbon atom.

If equivalent quantities of phenyl cyanate and the benzyl derivative of isobenzaldoxime, $O<\begin{matrix}N\cdot CH_2Ph\\ |\\ CHPh\end{matrix}$, are dissolved in benzene and the solution boiled, benzylphenylcarbamide, $NHPh\cdot CO\cdot NH\cdot CH_2Ph$, seems to be formed. But if the reaction is allowed to take place at the ordinary temperature, a residue is obtained when the benzene is evaporated which crystallises from alcohol in white needles melting at 121, and having the composition $C_{14}H_{18}N_2O_2$, that is, an additive compound of the cyanate and the oxime derivative. But it is not decomposed by boiling with acids or alkalis, and only when heated with concentrated hydrochloric acid in a sealed tube at 100° is it split up, yielding carbonic anhydride together with benzaldehyde and aniline hydrochloride, the last two substances crystallising together. The constitution of this substance is as yet undetermined.

C. F. B.

Two Different Modifications of Paranitrobenzylisobenzaldoxime. By R. BEHREND and E. KÖNIG (*Ber.*, **23**, 2750—2752).—When β-benzylparanitrobenzylhydroxylamine,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot N(CH_2Ph)\cdot OH,$$

is oxidised with ferricyanide of potassium, and the product crystallised from alcohol, *benzylisoparanitrobenzaldoxime*, $O<\begin{matrix}N\cdot CH_2Ph\\ |\\ CH\cdot C_6H_4\cdot NO_2\end{matrix}$, first separates out in brilliant, yellowish needles melting at 117—118°. The mother liquor then contains a substance which crystallises out in nodular aggregates melting at 93°; this consists of a mixture of equal parts of benzylisoparanitrobenzaldoxime and para-

nitrobenzylisobenzaldoxime, $O<\begin{matrix}N\cdot CH_2\cdot C_6H_4\cdot NO_2\\ |\\ CHPh\end{matrix}$. This compound cannot be decomposed by crystallisation from various solvents, but it was shown by Raoult's method to be completely dissociated when dissolved in acetic acid.

When paranitrobenzylisobenzylaldoxime is prepared from β-nitrobenzylhydroxylamine hydrochloride and benzaldehyde, a product is obtained which melts at temperatures varying between 105 and 114°, and is probably a mixture of two "physically" isomeric varieties of the oxime.

C. F. B.

Constitution of Carbonylorthamidophenol. By O. GRESSLY and M. NENCKI (*Monatsh.*, 11, 253—259; compare Abstr., 1883, 1110; 1887, 135, 245, 477).—The authors have sought to obtain evidence as to whether carbonylorthamidophenol (oxycarbamidophenol, hydroxymethenylamidophenol) has the constitution $C_6H_4<\begin{matrix}N\\ O\end{matrix}>C\cdot OH$ or $C_6H_4<\begin{matrix}NH\\ —O\end{matrix}>CO$, by investigating the changes which it undergoes in the animal system.

When an aromatic compound contains a carboxyl-group, it passes through the animal system either unchanged or as compounds of glycocine. The homologues of benzene, and the aromatic alcohols, aldehydes, and acids are oxidised in the side-chain, and mostly eliminated as carbonic anhydride. Hydroxy-compounds, especially when they contain no carboxyl group, and phenols are eliminated either as sulphates or as compounds of glyeurouie aeid. When the substance contains no hydroxyl or carboxyl group and undergoes no oxidation of the side-chain, a hydrogen atom in the benzene ring is displaced by hydroxyl; thus benzene is converted into phenol, indole into indoxyl, and so on. From this it will be seen that if the first of the above formulæ be correct carbonylorthamidophenol should undergo no further oxidation in the animal system, but should be eliminated either as a sulphate or as a compound of glycuronic acid; on the other hand, if the second formula be correct, a hydroxyl group should be substituted for a hydrogen atom in the benzene ring and some such compound as $OH\cdot C_6H_3<\begin{matrix}NH\\ —O\end{matrix}>CO$ should be obtained.

A rabbit received 1 gram of carbonylorthamidophenol per diem, in several doses, and a dog, of 12 kilograms body-weight, received 2—3 grams per diem in like manner. When 6 grams had been administered, the urine was evaporated to a syrup, acidified with hydrochloric acid until it contained 10 per cent. of acid, and heated for an hour in a reflux apparatus. When cold, the solution was shaken with ether, and the ether extract distilled. The residue is a new substance, earbonylortho-hydroxyamidophenol.

Carbonylortho-hydroxyamidophenol, $C_7H_5NO_3$, crystallises from hot water as a powder consisting of aggregates of microscopic rhombic prisms; it is easily soluble in alcohol and in alkaline solutions, from which it is precipitated by acids, and slightly in ether. It dissolves in

strong sulphuric acid unchanged, and is precipitated on addition of water. It decomposes with blackening at 265°. Its solution gives a characteristic red colour with chloride of lime, and a purple-red colour, becoming a red precipitate after a time, with Millon's reagent; these reactions can be obtained in urine itself after carbonylorthamidophenol has been administered. Its aqueous solution gives a greenish colour with ferric chloride. In the urine it mostly existed as a sulphate, especially, apparently, in the rabbit's urine; a little existed as a compound of glycuronic acid, and this was more plentiful in the dog's urine, a conclusion arrived at because a glycuronic acid compound would be more difficult to decompose by the hydrochloric acid treatment, and the yield of carbonylortho-hydroxyamidophenol would then be less, which was the case; moreover, the dog's urine reduced alkaline copper solution more strongly than the rabbit's urine did.

This formation of carbonylortho-hydroxyamidophenol is evidence in favour of the second formula for carbonylorthamidophenol.

A. G. B.

Silver Formanilide. By W. J. Comstock and F. Kleeberg (*Amer. Chem. J.*, **12**, 493—502).—This compound can be prepared by dissolving sodium formanilide in 50 per cent. alcohol, and gradually adding, with constant stirring, the theoretical quantity of silver nitrate, in dilute alcoholic solution; or, more quickly, by dissolving the theoretical quantities of formanilide and silver nitrate in dilute alcohol, and slowly stirring in the theoretical quantity of pure sodium hydroxide. When first precipitated, silver formanilide is an amorphous, white powder, which turns grey on exposure to light. It is quite stable at ordinary temperatures, and has the constitution NPh:CH·OAg, as shown by its behaviour with methyl iodide.

Methylisoformanilide, NPh:CH·OMe, is obtained when the above-described silver salt is treated with methyl iodide dissolved in a little ether. The resulting paste, on remaining, gradually becomes more fluid, and in 24 hours the reaction is complete. Ether is then added, and the solution filtered from silver iodide. On evaporating the ether, the compound is obtained as a heavy oil boiling at 196—198°. It is isomeric with formylmethylaniline; from which, however, it is easily distinguished, both by its odour, and by its giving with aniline the well-known diphenylformamidine, NPh:CH·NHPh.

Iodoisoformanilide is formed when finely pulverised silver formanilide is mixed with dry chloroform and 1 mol. of dry iodine is added. Silver iodide immediately forms, and is filtered off. The filtrate is concentrated first on a water-bath; afterwards, in a current of dry air, when a quantity of light-yellow crystals separates. These are washed with ether, and rapidly recrystallised from ether or chloroform. The compound is very unstable, and rapidly gives up iodine; water quickly decomposes it. In all probability, it has the constitution NH:CH·OI. The melting point could not be determined; but when slowly heated in a tube, very little iodine escapes, and the substance melts at 110°. In this case, however, a second compound, the result of molecular rearrangement, is formed.

Pariodoformanilide is obtained on heating iodoisoformanilide for a few minutes at 115°, or by simply adding formic acid to it. Crystallised from water, it forms white, transparent needles melting at 109—110°.

On dry distillation, silver formanilide yields symmetrical diphenylcarbamide, carbon monoxide, and metallic silver. G. T. M.

Derivatives of Aromatic Amines. By C. PAAL and G. OTTEN (*Ber.*, **23**, 2587—2599).—Butyric chloride reacts with sodacetanilide yielding butyranilide; benzoic chloride, under the same conditions, gives benzanilide.

Ethyl chlorocarbonate and sodacetanilide yield ethyl phenylcarbamate; ethyl chloromalonate is converted into ethyl dicarbinetetracarboxylate when it is treated with the sodium derivative of formanilide, acetanilide, or butyranilide.

Ethyl formanilidoacetate, COH·NPh·CH_2·COOEt, is obtained when a benzene solution of ethyl chloracetate is treated with sodioformanilide; it is a brown oil, and boils at 290—295°. The free *acid*, $C_9H_9NO_3$, prepared by hydrolysing the ethereal salt with concentrated alcoholic potash, crystallises from hot water in large, colourless needles, melts at 123—124°, and is readily soluble in ether, alcohol, glacial acetic acid, and concentrated mineral acids. The *sodium* salt, $C_9H_8NO_3Na$, is a crystalline, hygroscopic compound moderately easily soluble in alcohol.

Ethyl acetanilidoacetate, NPhAc·CH_2·COOEt, is formed when a benzene solution of ethyl chloracetate is treated with sodacetanilide; it is a yellow oil, boils at 298—300°, and solidifies to a mass of colourless plates when cooled. The free *acid* (m. p. 190—191) is obtained when the ethyl salt is hydrolysed with alcoholic potash; it has been previously prepared by Rebuffat (*Gazz. Chim.*, 17, 231). The *sodium* salt, $C_{10}H_{10}NO_3Na$, crystallises from dilute alcohol, and is very readily soluble in water. The *barium* salt, $(C_{10}H_{10}NO_3)_2Ba$ + $3H_2O$, crystallises from water in colourless needles. The copper salt is almost insoluble in water. The *bromo*-derivative,

$$C_6H_4Br·NAc·CH_2·COOH,$$

prepared by brominating the acid, crystallises from glacial acetic acid or dilute alcohol in colourless needles, and melts at 176—177°.

Acetoparatoluidoacetic acid, C_6H_4Me·NAc·CH_2·COOH, can be obtained by treating ethyl chloracetate with sodioparatoluidine, and hydrolysing the product with alcoholic potash. It crystallises from hot water in large plates, melts at 174—175°, and is almost insoluble in light petroleum, but more readily in hot ethyl acetate and alcohol. The *sodium* salt, $C_{11}H_{12}NO_3Na$ + $3H_2O$, crystallises from water in plates, and is very readily soluble.

α-Formanilidopropionic acid, COH·NPh·CHMe·COOH, is obtained when the reaction product of ethyl α-bromopropionate and sodioformanilide is hydrolysed with alcoholic potash. It crystallises from ether in large, colourless prisms, and is soluble in alcohol, ether, and hot water. The *barium* salt, $(C_{10}H_{10}NO_3)_2Ba$ + H_2O, is a crystalline powder readily soluble in water.

Ethyl α-acetanilidopropionate, NPhAc·CHMe·COOEt, prepared by heating sodioacetanilide with a benzene solution of ethyl α-bromopropionate, is a yellow oil boiling at 294—298°. The corresponding acid $C_{11}H_{13}NO_3$ has been previously prepared by Nastvogel (this vol., p. 1159). The *sodium* salt, $C_{11}H_{12}NO_3Na + 3H_2O$, is a crystalline compound readily soluble in water, but only sparingly in alcohol.

A compound which seems to have the composition $C_{12}H_{12}N_2$ is obtained in small quantities when sodioformanilide or sodacetanilide is suspended in benzene, heated with ethyl α-bromisobutyrate for several hours, and the oily product hydrolysed with alcoholic potash; it crystallises from dilute alcohol in yellow needles, melts at 130—132°, and is soluble in mineral acids; it is not identical with hydrazobenzene. A small quantity of the same substance (m. p. 130—132°) is obtained when ethyl β-iodopropionate or ethyl chloracetoacetate is treated with the sodium derivative of formanilide or acetanilide under the same conditions, and the product hydrolysed with alcoholic potash. F. S. K.

Oxidation of Ketones by Potassium Permanganate in Alkaline Solution. By C. Glücksmann (*Monatsh.*, **11**, 246—252; compare this vol., p. 237).—Acetophenone is easily oxidised to phenylglyoxylic acid under the following conditions:—A solution of potassium permanganate (32 grams) and potassium hydroxide (12 grams) in water (1 litre) is gradually added from a separating funnel to acetophenone (12 grams) suspended in water, with constant shaking; the solution must be kept cool with ice until it has become colourless, when it is filtered from the manganese dioxide, neutralised with sulphuric acid, and evaporated on the water-bath. The concentrated solution is shaken with ether to remove acetophenone, warmed to expel the ether which remains dissolved, and acidified with sulphuric acid to separate as much as possible of the benzoic acid which has been formed. After filtering, the filtrate is thoroughly extracted by ether, and this ethereal solution evaporated; the residue is dissolved in water, and shaken with carbon bisulphide, which extracts the rest of the benzoic acid, leaving a solution of phenylglyoxylic acid, which is crystallised in a vacuum. In two experiments, the yields were 20 and 22 per cent. respectively of the theoretical. The barium salt and phenylhydrazide were prepared so as to leave no doubt as to the identity of the acid.

Peter (Abstr., 1885, 764), Claus and Strohmenger (*Ber.*, **19**, 230), and Buchka (*Ber.*, **20**, 388) have failed to effect the oxidation of acetophenone to phenylglyoxylic acid by potassium permanganate; this the author attributes mainly to the fact that they did not use an excess of acetophenone, thus allowing the phenylglyoxylic acid to be further oxidised.

Buchka and Irish (Abstr., 1887, 483) used potassium ferricyanide, but attributed the formation of the small quantity of phenylglyoxylic acid which they obtained to a secondary reaction, and asserted that acetophenone oxidises according to Popoff's rule. Claus goes so far as to state (this vol., p. 769) that acetophenone cannot be oxidised to phenylglyoxylic acid by potassium permanganate under any circum-

stances, and, generally, that aromatic alkyl ketones can only be oxidised by potassium permanganate to ketonic acids when the benzene nucleus contains an alkyl group in the ortho-position relatively to the ketone group.

The author points out that the above statements must now be repealed; he suggests that Buchka and Irish would obtain a better yield in alkaline solution, and that Claus would succeed in oxidising many ketones to ketonic acids if he were to employ potassium permanganate in alkaline solution. A. G. B.

Isocinnamic Acid and Allocinnamic Acid. By C. LIEBERMANN (*Ber.*, 23, 2510—2515).—In preparing isocinnamic acid from the decomposition products of the alkaloïds occurring together with cocaïne (compare this vol., p. 494), the author has discovered a new acid, isomeric with isocinnamic acid, which he names allocinnamic acid. The material from which this new acid was isolated was a crude acid mixture obtained by decomposing the alkaloïds with hydrochloric acid and extracting the filtered solution with ether; this mixture was first boiled with dilute alkali to decompose ethereal salts, then further treated as previously described (*loc. cit.*), and the new acid finally separated from the isocinnamic acid by fractional crystallisation from hot light petroleum.

Allocinnamic acid, $C_9H_8O_2$, separates from light petroleum in colourless, monosymmetric crystals; $a : b : c = 1·5972 : 1 : 1·0300$; $\beta = 88° 38\frac{1}{2}'$; it melts at 68°, and is much more sparingly soluble in cold light petroleum than isocinnamic acid, which it resembles very closely in chemical behaviour. The *calcium* salt, $(C_9H_7O_2)_2Ca + 2H_2O$, prepared by neutralising the acid with calcium carbonate and evaporating the solution at 100°, crystallises in colourless needles, loses its water at 90°, and is rather more sparingly soluble than calcium isocinnamate. The *silver* salt, $C_9H_7O_2Ag$, is stable in the light. The acid is immediately oxidised to benzaldehyde by potassium permanganate; when distilled, it is converted into cinnamic acid, but the change takes place more slowly, and rather larger quantities of cinnamene and carbonic anhydride are produced than in the case of isocinnamic acid. When treated with iodine in carbon bisulphide solution, it is transformed into cinnamic acid, and bromine, under the same conditions, converts it into cinnamic acid dibromide. On reduction with sodium amalgam, it gives hydrocinnamic acid, but the change takes place rather more slowly, and a larger quantity of amalgam is required than is the case in the reduction of isocinnamic acid. It is partially converted into cinnamic acid by concentrated sulphuric acid, but about 80 per cent is resinified.

Both iso- and allo-cinnamic acids are gradually converted into cinnamic acid on exposure to direct sunlight, but the change takes place less rapidly in the case of the allo-acid; in this respect, the acids behave like the alkyl-substituted orthocoumaric acids investigated by Perkin (Trans., 1881, 409), the α-compounds corresponding with isocinnamic acid, and the β-compounds with cinnamic acid. When α-orthomethylcoumaric acid is heated at 90° with iodine (0·1 part) in

carbon bisulphide solution for five hours, it is almost completely transformed into the corresponding β-acid; the same change takes place when the α-compound is exposed to the light in alcoholic solution.

Isocinnamic chloride can be obtained by treating a well-cooled solution of the acid in light petroleum with phosphoric chloride; it is an unstable oil and gradually changes into the chloride of cinnamic acid.

Acid *aniline isocinnamate*, $2C_9H_8O_2,C_6H_7N$, is precipitated in long, colourless needles when light petroleum is added to a benzene solution of isocinnamic acid and aniline; it crystallises unchanged from boiling water, melts at 83°, and is only moderately easily soluble in cold water.

Isocinnamic acid seems not to be formed in the synthesis of cinnamic acid by Claisen's method (this vol., p. 891). F. S. K.

Dichlorosalicylic Acid. By J. L. HECHT (*Amer. Chem. J.*, **12**, 502—506).—The author finds that the three dichlorosalicylic acids, described by Rogers (*Inaug. Diss. Göttingen*, 1875), Smith (*Ber.*, **11**, 1225), and Pauli (*Inaug. Diss. Göttingen*, 1878) respectively, until now supposed to be isomerides, are identical, and yield the same dichlorophenol, [OH : Cl_2 = 1 : 2 : 4], on distillation with calcium oxide and sand. The only known dichlorosalicylic acid has consequently the constitution [COOH : OH : Cl_2 = 1 : 2 : 3 : 5]; it melts at 214°. G. T. M.

Action of Picric Chloride on Ethyl Sodacetoacetate. By E. DITTRICH (*Ber.*, **23**, 2720—2725).—When ethyl sodacetoacetate (1 mol.) in alcoholic solution is treated with picric chloride ($\frac{2}{3}$ mol.) and the solution evaporated, the residue contains *ethyl trinitrophenylacetoacetate*, $C_6H_2(NO_2)_3{\cdot}CHAc{\cdot}COOEt$, as well as the sodium derivative of this substance, $C_6H_2(NO_2)_3{\cdot}CNaAc{\cdot}COOEt$. By treatment with water the former is unaffected, whilst the latter dissolves, and its solution yields ethyl trinitrophenylacetoacetate itself when treated with dilute hydrochloric acid. This substance, when pure, forms yellow crystals melting at 98°, soluble in hot alcohol, ether, and benzene. With alkalis, it gives dark, reddish-brown solutions, from which dilute acids precipitate the original substance. It is decomposed when its aqueous solution is boiled. When treated with an equivalent quantity of sodium ethoxide, it yields the above-mentioned sodium derivative, which is a reddish-brown substance.

If, instead of $\frac{2}{3}$ mol. of picric chloride, 1 mol. is used, a sandy substance separates which is insoluble in most solvents, but crystallises from acetic acid in yellowish needles melting at 205° with decomposition; it is *ethyl ditrinitrophenylacetoacetate*,

$$CAc(C_6H_2[NO_2]_3)_2{\cdot}COOEt.$$

This is insoluble in cold aqueous alkalis; on warming, solution takes place, but the addition of acids does not reprecipitate the original substance. In alcoholic potash it dissolves, but when acids are added, ethyl trinitrophenylacetoacetate is precipitated, picric

acid having been formed. Small quantities of a substance melting at 80°, presumably ethyl ditrinitrophenylacetate, are also formed.

When a solution of ethyl trinitrophenylacetoacetate in acetic acid is boiled with sulphuric acid in a reflux apparatus, *trinitrobenzyl methyl ketone*, $C_6H_2(NO_2)_3 \cdot CH_2 \cdot COMe$, is formed. It crystallises from alcohol in long, yellowish needles melting at 89°, and dissolving in alkalis to reddish-brown solutions, from which acids reprecipitate the ketone. With phenylhydrazine, it yields a condensation product, $C_{15}H_{13}N_5O_6$, which forms brick-red prisms melting at 125° with decomposition. Only one of the nitro-groups could be reduced; further reduction being attended by decomposition. The reduction was effected by means of the equivalent quantity of stannous chloride. The product $C_9H_9N_3O_5$ when crystallised from alcohol, in which it is very soluble, forms groups of golden-yellow needles melting with decomposition at 214°. C. F. B.

Organic Sulphuretted Compounds. By A. PURGOTTI (*Gazzetta*, **20**, 24—32).—Otto (*Zeit. für Chemie*, **3**, 251) found that the action of sodium thiosulphate on benzyl chloride resulted in the formation of an impure brominated compound which on distillation with sulphuric acid yielded thiophenol, toluene, stilbene, thionessal, and tollalyl sulphide. When a solution of sodium thiosulphate (38 grams) in water (58 grams) is heated in a reflux condenser with a mixture of benzyl chloride (20 grams) and alcohol (40 grams) until the solutions intermingle, and the whole is then evaporated to dryness on the water-bath, a solid is left, which, after being purified by crystallisation from alcohol, forms white, nacreous tables, consisting of *sodium benzylthiosulphate*, $CH_2Ph \cdot S_2O_3Na$. This compound is very soluble in water, and the solution gradually decomposes on boiling; when heated with dilute hydrochloric acid, thiophenol is formed; on dry distillation, it decomposes with evolution of sulphurous anhydride, yielding benzyl bisulphide; on prolonged heating to 100—105°, it is decomposed into benzyl bisulphide and sodium dithionate. Amorphous *silver* and *mercury* salts and crystalline *barium* and *ammonium* salts may be prepared by double decomposition. On boiling a diluted alcoholic solution of the sodium salt with mercuric chloride, the compound $CH_2Ph \cdot SHgCl$ is formed.

Benzylthiosulphuric acid, $CH_2Ph \cdot S_2O_3H$, prepared from the barium salt crystallises from ether in colourless needles and prisms, and melts at 74—75°. It has a distinctly acid reaction, and is decomposed by boiling with water into thiophenol and sulphuric acid.

Chloranil dissolves in the cold in a concentrated solution of sodium thiosulphate, and on evaporation the solution leaves a black, amorphous residue, which is converted by boiling with hydrochloric acid into an insoluble, uncrystallisable, greenish-yellow compound having approximately the composition $C_6(OH)_2Cl(SH)_3$. This substance is readily soluble in alkalis, and is reprecipitated unchanged from its solutions on addition of hydrochloric acid. It is sparingly soluble in acetone.

When diazobenzene chloride is warmed with sodium thiosulphate, nitrogen is evolved, a red solution and a black oily compound remain-

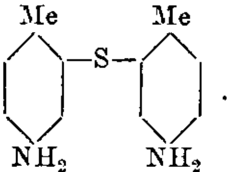
ing; the latter, on distillation in a current of steam. yields a mixture of phenyl sulphide and bisulphide; this is entirely converted into benzene sulphide on boiling it for four hours and redistilling. From the red solution, a compound having the composition $C_6H_8SN_2O_3$ and probably identical with Fischer and Romer's hydrazinebenzenesulphonic acid may be obtained. It crystallises in yellow needles.

When sodium sulphide is gradually added to paradiazotoluene, a violent action ensues and the liquid must be kept cold to avoid an explosion. The product is a yellow oil which, on distillation, yields a crystalline compound containing cresyl parasulphide and parahydrosulphide.

Sodium sulphide has a similar action on orthodiazotoluene, cresyl orthosulphide and hydrosulphide being formed; the former is a liquid boiling at 285°, and readily soluble in chloroform, ether, and carbon bisulphide, but only sparingly in alcohol and in acetic acid. The *mercuric salt* of the hydrosulphide, $(C_6H_4MeS)_2Hg$, crystallises in white needles, the *ethyl* salt, $C_6H_4Me{\cdot}SEt$, obtained by converting the hydrosulphide into a sodium salt and boiling with ethyl iodide and alcohol, is a heavy liquid which boils at 120°, and has an odour of onions.

Orthocresylethylsulphine, $S(C_6H_4Me)_2EtI$, prepared by heating orthocresyl sulphide with ethyl iodide, is an insoluble compound crystallising in needles; *orthocresylsulphone*, $SO_2(C_6H_4Me)_2$, obtained by oxidising a dilute acetic acid solution of the sulphide with potassium permanganate, crystallises in needles melting at 134—135°.

When Merz and Weith's thioparatoluidine (Abstr., 1871, 566) is diazotised and the product heated with alcohol, it is decomposed with evolution of nitrogen, and on adding water to the residue, cresyl orthosulphide is precipitated; the constitution of thioparatoluidine is, therefore,



S. B. A. A.

Phenyldithienyl. By A. RENARD (*Compt. rend.*, **111**, 48—49).—Phenyldithienyl is obtained, together with phenylthiophen, by the action of sulphur on toluene at a dull red heat (this vol., p. 134). That portion of the product which is least soluble in alcohol is exhausted with benzene, and the phenyldithienyl which dissolves is purified by recrystallisation from pure benzene. It has the composition $C_4SH_2Ph{\cdot}C_4SH_3$, and forms colourless plates which melt at 209°, sublime easily, and are almost insoluble in alcohol, ether, and light petroleum, slightly soluble in chloroform or ethyl acetate, and very soluble in boiling benzene or toluene. With isatin and sulphuric acid, phenyldithienyl gives a blue coloration, and with phenanthraquinone, a green coloration. It is not attacked by alkaline or neutral permanganate, but is completely oxidised by chromic anhydride in acetic acid. If the acetic acid is previously diluted with an equal volume of water, a small quantity of benzoic acid is formed. *Tribromphenyldithienyl*, $C_{14}S_2H_7Br_3$, is obtained by treating phenyldithienyl with

excess of bromine and leaving it exposed to the air until the hydrogen bromide and excess of bromine have escaped. The residue is boiled with alcoholic potash, washed with water, dried, and crystallised from carbon bisulphide. It forms white crystals which melt at 320°, are almost insoluble in alcohol, benzene, and chloroform, and slightly soluble in carbon bisulphide. With isatin and sulphuric acid, it gives no coloration. *Dinitrophenyldithienyl* is obtained by the action of ordinary fuming nitric acid and is purified by washing it with ammonium carbonate solution, water, and alcohol. It forms a yellow powder which melts at 273°, is insoluble in ether and light petroleum, very slightly soluble in alcohol, ethyl acetate, and chloroform, and somewhat more soluble in benzene. It gives no coloration with isatin and sulphuric acid, but, like the dinitrothiophens, when treated with an alkaline hydroxide in presence of alcohol, it gives a red coloration which is discharged by acids. *Phenyldithienyldisulphonic acid*, $C_{14}S_2H_8(SO_3H)_2$, is obtained by the action of fuming sulphuric acid in the cold, or of the ordinary acid at 150°. Its barium salt forms colourless crystals very soluble in water. C. H. B.

Methylation of the Indoles. By E. Fischer and J. Meyer (*Ber.*, **23**, 2628—2634).—It has previously been shown by E. Fischer and Steche (Abstr., 1888, 298) that 2′-methylindole is converted by methyl iodide into a compound, for which they found the formula $C_{11}H_{13}N$, and which from its behaviour appeared to be a derivative of dihydroquinoline, having the formula $C_6H_4<\begin{matrix}CH{=}CMe\\ NMe{\cdot}CH_2\end{matrix}$. They found further that 2′ : 3′-dimethylindole also yields dihydroquinoline derivatives closely resembling the above compound. The renewed investigation of the subject by the authors has shown that the compound obtained from 2′-methylindole and methyl iodide has the formula $C_{12}H_{15}N$ instead of $C_{11}H_{13}N$, and that it is identical with the compound obtained from 2′ : 3′-dimethylindole. It must therefore be a trimethyldihydroquinoline, and not, as previously supposed, a dimethyl derivative.

In the preparation of trimethyldihydroquinoline, the method previously given was adhered to. The numbers required for the formulæ $C_{11}H_{13}N$ and $C_{12}H_{15}N$ do not differ sufficiently to allow of any conclusion as to composition being drawn from the analysis, but by the action of hydrogen iodide in ethereal solution, the base yields a crystalline *hydriodide*, which, from a determination of the iodine, must have the formula $C_{12}H_{15}N,HI$. As above stated, it is obtained in a similar manner from 2′ : 3′-dimethylindole, and may also be prepared, although with greater difficulty, from scatole and 1′-methylindole. On reduction with tin and hydrochloric acid, it readily yields trimethyltetrahydroquinoline (previously described as a dimethyl compound). This yields a well-crystallised *methiodide*, the analysis of which showed its composition to be $C_{12}H_{17}N,MeI$.

The formation of trimethyldihydroquinoline is represented by the equation $C_9H_9N + 3CH_3I = C_{12}H_{15}N + 3HI$. One of the methyl groups enters as methylene into the indole ring, a second combines with the nitrogen, whilst the third unites with one of the carbon

atoms of the indole ring. The methylene group may either enter into the ring between the nitrogen and carbon atoms, or between the doubly-linked carbon atoms, giving a choice between the three formulæ:—

$$C_6H_4<\begin{matrix}CMe\colon CMe\\ NMe\cdot CH_2\end{matrix};\quad C_6H_4<\begin{matrix}CMe\colon CH\\ NMe\cdot CHMe\end{matrix};\quad C_6H_4<\begin{matrix}CHMe\cdot CH\\ NMe-CMe\end{matrix}.$$

An attempt was made to ascertain which of these formulæ is correct by converting 2′ : 4′-dimethylquinoline and 3′ : 4′-dimethylquinoline into the corresponding trimethyltetrahydroquinolines, and comparing them with the compound obtained by the reduction of trimethyldihydroquinoline. It was found, however, that all three compounds are different, that obtained from 2′ : 4′-dimethylquinoline melting 40°, and that from 3′ : 4′-dimethylquinoline 59°, lower than the compound from trimethyldihydroquinoline. No conclusion as to the position of the methyl groups can therefore be obtained in this manner.

H. G. C.

Derivatives of Diphenylmethane and Benzophenone. By W. Staedel and E. Haase (*Ber.*, **23**, 2577—2579).—The authors give in tabular form the names and melting points of the various nitro-, amido-, acetamido-, and hydroxy-compounds which they have prepared from diphenylmethane and benzophenone (compare Abstr., 1883, 990).

F. S. K.

Reduction of Nitriles. By M. Freund and P. Remse (*Ber.*, **23**, 2859—2865; compare this vol., p. 1388).—Dibenzyl is prepared by dissolving α-phenylcinnamonitrile (30 grams) in alcohol, and gradually adding sodium (70 grams), so that a regular, steady evolution of hydrogen takes place; the product is treated with water and distilled in a current of steam, the solid portion of the distillate is washed with hydrochloric acid, and crystallised from alcohol; the yield is 75 per cent. of theory. On treating the nitrile with 2·5 parts of sodium and allowing the reaction to proceed as quickly as possible, *diphenylpropylamine*, $CH_2Ph\cdot CHPh\cdot CH_2\cdot NH_2$, is formed; it is a colourless, viscid liquid which boils at 315—317°, and is miscible with alcohol, chloroform, or ether. The *hydrochloride* is deposited from concentrated hydrochloric acid in white needles melting at 188—190°. The *platinochloride* forms pale-yellow crystals which decompose at 153°. The *aurochloride* crystallises in golden-yellow plates melting at 144—145°. The *mercurochloride* is obtained as a white, crystalline powder which melts at 107°. *Diphenylpropylcarbamide*,

$$CH_2Ph\cdot CHPh\cdot CH_2\cdot NH\cdot CO\cdot NH_2,$$

is prepared by the action of potassium cyanate on the hydrochloride; it crystallises in slender, white needles melting at 112°. *Diphenylpropylphenylthiocarbamide*, $CH_2Ph\cdot CHPh\cdot CH_2\cdot NH\cdot CS\cdot NHPh$, crystallises from alcohol in colourless cubes melting at 129°. *Diphenylpropyloxamide*, $C_2O_2(NH\cdot CH_2\cdot CHPh\cdot CH_2Ph)_2$, is formed by the action of ethyl oxalate on the free base, and is deposited from alcohol in white crystals which melt at 115—116°. *Diacetyldiphenylpropylamine*,

$CH_2Ph\cdot CHPh\cdot CH_2\cdot NAc_2$, is prepared by the action of sodium acetate and acetic anhydride; it crystallises from alcohol in slender, white needles melting at 85°. *Diphenylpropyl alcohol*, $CH_2Ph\cdot CHPh\cdot CH_2\cdot OH$, is obtained on treating the amine hydrochloride with silver nitrite; it is a slightly yellow, viscid liquid boiling at 300—302°.

β-Phenyl-γ-anisylpropylamine, $OMe\cdot C_6H_4\cdot CH_2\cdot CHPh\cdot CH_2\cdot NH_2$, is prepared by the action of sodium on phenylanisacrylonitrile in alcoholic solution; it is a yellow, oily liquid, and decomposes on distillation; the *hydrochloride* is also unstable. The *platinochloride* crystallises from water in small, yellow needles which melt at 195° with decomposition. The *aurochloride* is deposited in golden-yellow plates melting at 87°. If the reduction of α-phenylanisacrylonitrile is effected more slowly, *phenylanisylethane*, $CH_2Ph\cdot CH_2\cdot C_6H_4\cdot OMe$, is formed; it is soluble in ether, chloroform, or benzene, and crystallises from alcohol in colourless plates melting at 61°; the yield is 57 per cent. of the nitrile employed. J. B. T.

Triphenylbenzene. By E. Mellin (*Ber.*, **23**, 2533—2536).—Benzoic acid (0·6 gram) is formed when triphenylbenzene (1 gram) is oxidised with chromic acid in warm glacial acetic acid solution.

Dodecahydrotriphenylbenzene, $C_{24}H_{30}$, can be prepared by heating triphenylbenzene at 270—280° for 16 hours with hydriodic acid and amorphous phosphorus. It is an oil with an aromatic odour, and it gradually solidifies in the cold; it is not acted on by cold concentrated nitric acid, but on warming nitro-derivatives are formed. It is converted into sulphonic acids by hot fuming sulphuric acid, but no action takes place in the cold; on oxidation with chromic acid in boiling glacial acetic acid solution, it yields benzoic acid.

Eikosihydrotriphenylbenzene, $C_{24}H_{38}$, is obtained as an oil when the reduction of triphenylbenzene under the above conditions is allowed to proceed for 32 hours.

Tetranitrotriphenylbenzene, $C_{24}H_{14}(NO_2)_4$, is formed, together with an isomeride melting at 108° (see below), when triphenylbenzene is nitrated in glacial acetic acid solution. It crystallises from nitrobenzene, aniline, and ethyl benzoate in pale yellow needles, melts above 370°, and is only very sparingly soluble in all ordinary solvents.

The *tetramido*-derivative, $C_{24}H_{14}(NH_2)_4$, prepared by reducing the nitro-compound with tin and hydrochloric acid in glacial acetic acid solution, crystallises from alcohol in small, colourless needles, and melts at 137—138°. The *octacetyl*-derivative, $C_{24}H_{14}(NAc_2)_4$, is formed when the amido-compound is boiled for six hours with sodium acetate and glacial acetic acid; it crystallises in colourless, microscopic needles, and melts at 156—158°.

Tetranitrotriphenylbenzene, $C_{24}H_{14}(NO_2)_4$, remains in the acid mother liquors from the nitro-compound described above, and is precipitated on the addition of water; it crystallises from alcohol in small needles, melts at 108° with decomposition, and is soluble in ether, alcohol, benzene, and glacial acetic acid. The *tetramido*-compound, $C_{24}H_{14}(NH_2)_4$, crystallises from dilute alcohol in yellowish needles, melts at 96—98° with decomposition, and rapidly darkens on exposure to the air. The *octacetyl*-derivative, $C_{24}H_{14}(NAc_2)_4$, separates from dilute acetic acid

in granular crystals, melts at 142—143°, and is soluble in alcohol and ether.

Triphenylbenzenedisulphonic acid was prepared by treating the hydrocarbon with fuming sulphuric acid at 100°; the *barium* salt, $C_{21}H_{16}(SO_3)_2Ba$, crystallises from very dilute alcohol in small, colourless plates. F. S. K.

Constitution of Naphthalene. By A. CLAUS (*J. pr. Chem.* [2], **42**, 24—49).—In this paper, the author criticises the views recently put forward by Bamberger (this vol., p. 1299); he admits the probability that one of the nuclei in naphthalene is a benzene ring, and proceeds to discuss the structure of the naphthalene derivatives on the supposition that they contain his "diagonal" benzene ring.

A. G. B.

Constitution of Dinitro-β-naphthol. By E. LOEWE (*Ber.*, **23**, 2542—2546).—*Barium dinitro-β-naphthol*, $[C_{10}H_5(NO_2)_2 \cdot O]_2Ba + H_2O$, is obtained when a solution of potassium dinitro-β-naphthol, prepared as described by Graebe and Drews (Abstr., 1884, 1035), is treated with barium chloride; it crystallises in orange needles, and loses its water at 100°.

Diamido-β-naphthol hydrochloride, $OH \cdot C_{10}H_5(NH_2)_2,2HCl$, prepared by reducing the nitro-compound with tin and hydrochloric acid, crystallises in almost colourless needles; the free base readily oxidises on exposure to the air. The *triacetyl* derivative, $OAc \cdot C_{10}H_5(NHAc)_2$, crystallises from glacial acetic acid in small needles, melts at 203°, and is sparingly soluble in alcohol, and insoluble in water. The *tribenzoyl* derivative, $OBz \cdot C_{10}H_5(NHBz)_2$, crystallises from glacial acetic acid in colourless plates, melts at 265°, and is only sparingly soluble in alcohol and water.

Diamido-β-naphthylamine hydrochloride, obtained by reducing dinitro-β-naphthylamine (compare Graebe and Drews, *loc. cit.*) with tin and hydrochloric acid, crystallises from water in yellowish needles which, after being kept for a long time over soda-lime, have the composition $C_{10}H_5(NH_2)_3,2HCl$. The *sulphate*, $2C_{10}H_5(NH_2)_3,3H_2SO_4$, is crystalline, and only very sparingly soluble in boiling water. The *triacetyl* derivative, $C_{10}H_5(NHAc)_3$, crystallises from glacial acetic acid in colourless needles, and melts at 280° with decomposition. The *tribenzoyl* derivative, $C_{10}H_5(NHBz)_3$, crystallises in yellowish needles, melts at 277°, and is sparingly soluble in alcohol and water.

Amidonaphthaphenanthrazine, $C_{24}H_{15}N_3$, is formed by the condensation of diamido-β-naphthylamine and phenanthraquinone in warm glacial acetic acid solution. It separates from aniline in golden crystals, and dissolves in hydrochloric acid with a reddish-brown, and in concentrated sulphuric acid with a violet coloration; it sublimes readily, and its ethereal solution is fluorescent. The formation of this compound proves that one of the nitro-groups in dinitro-β-naphthol is in the ortho-position relatively to the hydroxyl group.

F. S. K.

Theory of the Truxillic Acids. By C. LIEBERMANN (*Ber.*, **23**, 2516—2518).—The author points out that, assuming that the truxillic acids are tetramethylene derivatives, and applying the principles laid

down by Baeyer in his discussion of the constitution of hexamethylene derivatives to the tetramethylene ring, there are 11 theoretically possible truxillic acids, four of which are already known; the constitution of the isomerides is given. F. S. K.

Formation of Anthraquinone under certain Conditions. By L. H. FRIEDBURG (*Chem. Centr.*, 1890, ii, 9; from *J. Amer. Chem. Soc.*, **12**, 26—43).—In the reaction between phenanthraquinone, α-thiotolen, and concentrated sulphuric acid, the dye formed reacts with lead chromate, forming anthraquinone, and the author considers it probable that this is formed exclusively from the thiotolen, and not from the phenanthraquinone. J. W. L.

Benzyloxanthranol. By C. BACH (*Ber.* **23**, 2527—2530; compare this vol., p. 1144).—*Benzyloxanthranol chloride*,

$$C_6H_4<\begin{matrix}CCl(C_7H_7)\\CO\cdot C_6H_4-\end{matrix}>,$$

is formed when finely-divided benzyloxanthranol is treated with phosphoric chloride. It crystallises from light petroleum in colourless plates, melts at 95—102°, and is soluble in benzene, yielding a solution which shows a blue fluorescence; it dissolves in concentrated sulphuric acid with a red coloration, and it is readily decomposed by water.

Benzyldihydroanthranol, $C_6H_4<\begin{matrix}CH(C_7H_7)\\CH(OH)-\end{matrix}>C_6H_4$, prepared by reducing benzyloxanthranol with zinc-dust and ammonium hydrate, or with sodium amalgam in alcoholic solution, crystallises from a mixture of benzene and light petroleum in yellowish needles, decomposes at 130—140°, and readily oxidises on exposure to the air; it dissolves in concentrated sulphuric acid yielding a yellow solution which quickly turns green, and, when boiled with dilute acetic acid, it is decomposed quantitatively into benzylanthracene and water.

Benzylanthranol, $C_6H_4<\begin{matrix}C(C_7H_7)\\C(OH)-\end{matrix}>C_6H_4$, can be obtained by treating bromobenzyleneanthrone (bromodihydrobenzyloxanthranol) with sodium amalgam in cold alcoholic solution; it crystallises from benzene in yellow needles, melts at 183—184°, is readily soluble in alcohol, ether, and glacial acetic acid, and dissolves in concentrated sulphuric acid with a yellow coloration; it is oxidised to benzyloxyanthranol on exposure to the air.

Ethoxybenzyleneanthrone, $C_6H_4<\begin{matrix}C(CPh\cdot OEt)\\CO\cdot C_6H_4-\end{matrix}>$, prepared by warming bromobenzyleneanthrone with sodium ethoxide in alcoholic solution, crystallises from alcohol in yellow plates, melts at 171—173° with decomposition, and is readily soluble in ether, alcohol, benzene, and glacial acetic acid; it dissolves in concentrated sulphuric acid yielding a blood-red solution.

Amidobenzyleneanthrone, $C_6H_4<\begin{matrix}C(CPh\cdot NH_2)\\CO\cdot C_6H_4-\end{matrix}>$, is precipitated as an oil, when anhydrous ammonia is passed into a benzene solution of

bromobenzyleneanthrone; it separates from a mixture of benzene and light petroleum as an amorphous, orange powder, melts at 150—152°, and dissolves in concentrated sulphuric acid with a violet-red coloration.

Benzylanthracene dihydride, $C_6H_4<\begin{matrix}CH(C_7H_7)\\CH_2\cdot C_6H_4\end{matrix}>$, is obtained when benzylanthracene is reduced with sodium amalgam in boiling alcoholic solution, or with hydriodic acid and amorphous phosphorus; it crystallises from alcohol in prismatic needles, melts at 110—111°, and dissolves in warm concentrated sulphuric acid with a dark-green coloration. F. S. K.

Mesoanthramine. By F. Goldmann (*Ber.*, **23**, 2522—2526).—*Mesoanthramine*, $C_6H_4<\begin{matrix}C(NH_2)\\|\\CH\cdot C_6H_4\end{matrix}>$, can be obtained by heating finely-divided anthranol at 200° for about 22 hours with concentrated aqueous ammonia (20 parts); it is purified by converting it into the hydrochloride. It crystallises from cold, dilute alcohol in golden plates, darkens on exposure to the air, and decomposes at about 215°; it is only very sparingly soluble in boiling water, but very readily in ether, benzene, alcohol, and chloroform, the yellow solutions showing a green fluorescence. On oxidation with chromic acid in glacial acetic acid solution, it is converted into anthraquinone. The *hydrochloride*, $C_{14}H_9\cdot NH_2,HCl$, crystallises in colourless needles, is only sparingly soluble in alcohol and boiling hydrochloric acid, and is decomposed by cold water or on exposure to the air; on adding diazobenzenesulphonic acid to a cold alcoholic solution of this salt, a magenta-red coloration is immediately produced, and then a red precipitate, which is insoluble in water and alcohol, but soluble in dilute ammonia, yielding a greenish-yellow solution. The *acetyl* derivative, $C_{14}H_9\cdot NHAc$, prepared by dissolving the base in cold acetic anhydride, crystallises from alcohol in colourless needles, melts at 273—274°, and is rather sparingly soluble in alcohol and benzene; it is very stable, and, when boiled with alcoholic potash, yields a yellow, crystalline compound—probably the potassium derivative—which, when treated with water, is reconverted into the acetyl derivative.

The *diacetyl* derivative, $C_{14}H_9\cdot NAc_2$, obtained by boiling the base with acetic anhydride, crystallises from dilute alcohol in colourless plates, melts at 159°, and is readily soluble in most ordinary solvents except water; it is converted into the monacetyl derivative by boiling alcoholic potash.

Mesoanthramine hydride, $C_{14}H_{11}\cdot NH_2$, is formed when mesoanthramine is boiled with sodium amalgam in alcoholic solution; it crystallises from dilute alcohol in colourless needles, melts at 92°, and is readily soluble in alcohol, ether, and benzene. The hydrochloride, $C_{14}H_{11}\cdot NH_2,HCl$, crystallises in colourless needles, and is readily soluble in water; when an aqueous solution of this salt is boiled with hydrochloric acid, it is decomposed quantitatively into anthracene and ammonia. F. S. K.

Rotatory Power of Camphor when Dissolved in Various Oils. By P. CHABOT (*Compt. rend.*, **111**, 231—233).—The rotatory power of solutions of camphor in olive oil, oil of sweet almonds, and grape-seed oil is practically proportional to their concentration. If p = the percentage amount of camphor in the solution, and α the rotatory power for D, of a column 20 cm. long, then, with olive oil, $\alpha = 10' + p\ 1°\ 1'$; with almond oil, $\alpha = p$; and with grape-seed oil, $\alpha = 36' + p$. Saturated solutions contain the following percentage amounts of camphor: olive oil, 26·93; almond oil, 28·53; and grape-seed oil, 28 80. The molecular rotatory powers of camphor in solution of the three oils are as follows:—

	Olive oil.	Almond oil.	Grape-seed oil.
3 per cent.	55° 42′	56° 47′	54° 24′
20 per cent.	55 12	54 19	54 7

The molecular rotatory power varies little with the concentration, but, as usual, is greater in more dilute solutions. C. H. B.

Combination of Camphor with Phenols. By E. LÉGER (*Compt. rend.*, **111**, 109—111).—Camphor and the phenol are melted together in the calculated proportions in closed vessels. Under these conditions, compounds are formed which decompose easily under the influence of heat, or when treated with solvents or with alkalis. That definite compounds are formed is, however, shown by the fact that the liquid products contain their constituents in molecular proportions, and that in those cases where they crystallise the composition of the first crystals is the same as that of the last. The addition of phenols to alcoholic solutions of camphor reduces the rotatory power of the latter to one-half. The compositions of the various products were determined by means of the polarimeter, and the method will be described in detail subsequently.

Phenol monocamphoride, $C_6H_6O,C_{10}H_{16}O$, is a colourless liquid, which crystallises only at about −23°; sp. gr. at about 0° = 1·0205; $[\alpha]_D = +20°$. *Phenol hemicamphoride*, $2C_6H_6O,C_{10}H_{16}O$, a colourless liquid which does not solidify at −50°; sp. gr. at 0° = 1·040; $[\alpha]_D = +10°·5$. It combines with camphor to form the monocamphoride; if mixed with excess of phenol, the latter dissolves, but when the liquid is cooled to −25°, it separates distinctly into phenol hemicamphoride and phenol. *Resorcinol monocamphoride*, $C_6H_6O_2,C_{10}H_{16}O$, forms large, thin, hygroscopic, rectangular lamellæ, which become liquid when mixed with a small quantity of water, and are decomposed by a large quantity with separation of camphor. It melts at about 29°, but can remain for a long time in superfusion at 15°; rotatory power in alcoholic solution, $[\alpha]_D = +22·5°$. *Resorcinol dicamphoride*, a syrupy, colourless liquid, which forms large, hexagonal crystals at 0°; sp. gr. at 15° = 1·0366; $[\alpha]_D = +25·9°$. *α-Naphthol camphoride*, $C_{10}H_8O,C_{10}H_{16}O$, is a slightly coloured, syrupy liquid, which does not solidify at −16°, and is not decomposed by water; sp. gr. at 0° = 1·0327; $[\alpha]_D = +10·5°$. It dissolves α-naphthol, which separates in short, rhombic prisms (Wyrouboff). *β-Naphthol camphoride*, $3C_{10}H_8O,5C_{10}H_{16}O$, a liquid very similar to

the preceding compound, sp. gr. at 0° = 1·0396; $[\alpha]_D$ = +22·5°. It dissolves β-naphthol, which separates from it in somewhat large, tabular crystals. *Salicylic camphoride*, $C_7H_6O_3,2C_{10}H_{16}O$, a white, nacreous mass of long, thin, microscopic needles, which melts at about 0°, and is only partially decomposed even by boiling water. Its rotatory power in alcoholic solution is $[\alpha]_D$ = +27·3°.

Salol seems to form a similar compound, but its composition has not yet been determined. Salol crystallises from salol camphoride in bulky, irregular crystals of the rhombic system, and some measurements of these by Wyrouboff are given. C. H. B.

Russian Oil of Peppermint. By H. ANDRES (*Chem. Centr.*, 1890, ii, 63; from *Pharm. Zeit. Russ.*, **29**, 341—343).—The oil which the author examined was obtained from the fresh plant. It is greenish-yellow; sp. gr. = 0·915 at 15°; $[\alpha]_D$ = −17·13°. The principal distillates are obtained at 160—165°, 173—175°, 203—206°, and 206—209°. The fraction passing over between 173—175° has the highest specific rotation, and contains the terpene $C_{10}H_{16}$; sp. gr. = 0·8667 at 4°, and = 0·8571 at 20° (water at 4° = 1); specific rotation in 10 cm. tube at 20° = $[\alpha]_D$ = −41·19°. The tetrabromide of this terpene melts at 102°; $[\alpha]_D$ = −18·71°; the inactive dihydrochloride, $C_{10}H_{16},2HCl$, melts at 50°; the nitrosyl chloride, $C_{10}H_{16}NOCl$, melts at 103°, and has the specific rotation −205·28°. These reactions, together with the properties of the levorotatory nitrosoterpenes melting at 72°, prove the identity of the terpene of oil of peppermint with the terpenes which Wallach (Abstr., 1889, 1069) has described. The fraction 160—165° consists of a mixture of terpene and menthene, $C_{10}H_{18}$. The presence of the latter is proved by the preparation of the dibromomenthene $C_{10}H_{18}Br_2$ and the chloromenthyl $C_{10}H_{19}Cl$ (K_{100} = 130—140°; sp. gr = 0·9381 at 20°). From the fractions 203—206° and 206—209°, menthone and menthol are obtained. Hydroxylamine unites with the former forming menthoxime, by which means the two compounds are separated. Hydrochloric acid liberates menthone from the oxime; it boils at 206—208°; sp. gr. = 0 8998, 20/20°; $[\alpha]_D$ = +8·04. J. W. L.

Conversion of Pyrroline into its Homologues. By M. DENNSTEDT (*Ber.*, **23**, 2562—2574).—When a mixture of the vapours of pyrroline and alcohol is passed over heated zinc-dust, a liquid consisting of various homologues of pyrroline is obtained, and a large quantity of ethylene is evolved. The experiment was carried out in the following manner:—A long glass tube is bent at a right angle, and the shorter limb is loosely filled with copper turnings, in the longer limb zinc-dust being placed in such a way that it forms a layer occupying about one-third of the breadth of the tube. The longer limb is then heated in a combustion furnace at about 270—280°, and a mixture of equal volumes of alcohol and pyrroline dropped into the shorter limb, which is placed vertically and connected by means of a cork with a stoppered funnel; the products are collected in a receiver provided with a reflux condenser. With an apparatus

of this kind, 100—120 c.c. of the liquid mixture can be treated without renewing the zinc-dust.

The liquid in the receiver begins to boil at about 60°; the portion passing over below 135° was employed in subsequent operations; the remainder, after repeated fractional distillation, was separated into the following constituents, 100 grams of pyrroline having been employed.

(1.) A liquid (15 grams) boiling at 163—165°, which is identical with the ethylpyrroline obtained by Ciamician and Zanetti (Abstr., 1889, 727) from pyrroline and ethyl iodide.

(2.) A liquid (3 to 5 grams) boiling at 175—177°, which consists of a mixture of ethyl- and diethyl-pyrroline.

(3.) A diethylpyrroline (8 to 10 grams) boiling at 185—187°, which, when heated with acetic anhydride and sodium acetate at 190°, yields an *n*-acetyl and a *c*-acetyl-derivative; the latter separates from benzene or dilute alcohol in monosymmetric crystals, melts at 98°, and boils at about 295—300°.

(4.) A triethylpyrroline (5 grams) boiling at 200—205°, which yields an *n*-acetyl and a *c*-acetyl-derivative; the latter separates from alcohol in well-defined monosymmetric crystals, melts at 138°, and boils above 300°.

(5.) A liquid (5 grams) boiling at 210—240°, the nature of which has not yet been determined.

Methyl alcohol and pyrroline give products analogous to those obtained from ethyl alcohol and pyrroline under the same conditions, but the various compounds have not been completely separated from one another.

When benzene is heated with alcohol in the manner described above, only very small quantities of higher-boiling hydrocarbons are formed, and the products cannot be isolated except with great difficulty. Phenol under the same conditions gives small quantities of at least two ethyl phenols; aniline reacts both with methyl and ethyl alcohol, yielding considerable quantities of methyl- and ethyl-aniline, benzonitrile being also formed when methyl alcohol is employed.

When a mixture of the vapours of pyridine and ethyl alcohol is passed over heated zinc-dust, small quantities of α-ethylpyridine and $\alpha\gamma$-diethylpyridine are formed, but most of the pyridine remains unchanged.

Piperidine reacts with alcohol much more readily than pyridine, about 50 per cent. of the base being changed; the following compounds were isolated from the reaction product:—(1.) Considerable quantities of *n*-ethylpiperidine boiling at 128°. The *platinochloride*, $(C_7H_{15}N)_2,H_2PtCl_6$, forms bright-red, well-defined crystals, melting at 202°. The *aurochloride*, $C_7H_{15}N,HAuCl_4$, separates from dilute hydrochloric acid in dark-yellow crystals, and melts at 106—107°. The *picrate*, $C_7H_{15}N,C_6H_3N_3O_7$, crystallises from hot water, and melts at 163°.

(2.) Very small quantities of two liquids boiling at 140—146° and 152—158° respectively, the nature of which was not determined.

(3.) A rather larger quantity of a liquid boiling at 165—175°,

which is a mixture of two diethylpiperidines. The two compounds can be separated by means of their picrates, both of which have the composition $C_9H_{19}N,C_6H_3N_3O_7$; the one crystallises in long needles melting at 89—90°, the other forms small compact crystals melting at 105—107°.

(4.) A diethylpiperidine boiling at 180—190°, the hydrochloride of which is deliquescent; the aurochloride is an oil, but the picrate crystallises from water in long, yellow needles, and melts at 75—76°.

F. S. K.

Derivatives of Dihydropyrroline. By F. ANDERLINI (*Gazzetta*, **20**, 69—73).—*Dihydropyrroline hydrochloride*, described by Ciamician and Dennstedt, forms a deliquescent, crystalline mass, which decomposes on heating with evolution of vapours which give the pinewood reaction. It is decomposed by heating with concentrated hydrochloric acid at 130—140°, and is probably converted in part into pyrroline. The *aurochloride*, $C_4NH_7,HAuCl_4$, may be obtained in orange-yellow crystals by concentrating its solution in dilute hydrochloric acid in a vacuum, but it is partially decomposed when heated on the water-bath. It melts at 152°, and is freely soluble in water; the *picrate* is a yellow salt, freely soluble in water or alcohol, and melts at 156°.

Benzoyldihydropyrroline.—When dihydropyrroline hydrochloride (3 grams) is heated with benzoic chloride (8 grams) for about seven hours at 110°, the product is a brown syrup from which a portion distilling between 160° and 161° under a pressure of about 2 mm. may be separated by fractionation. This portion has the composition C_4NH_6Bz. It is a heavy, aromatic oil, soluble in ether but not in water; it dissolves in hydrochloric acid forming a difficultly crystallisable hydrochloride, which yields yellow oily compounds with platinic and auric chlorides, with picric acid, and with the double iodide of potassium and mercury or cadmium, and a white precipitate with mercuric chloride.

Acetic chloride acts on dihydropyrroline in a different way from benzoic chloride, the products of the reaction being a complex mixture of various compounds.

Benzylhydropyrroline.—When dihydropyrroline is treated with benzyl chloride, and the solid product of the reaction separated and fractionally distilled, a small quantity of an oily liquid passes over at about 150°. This fraction is insoluble in water, but dissolves in dilute hydrochloric acid. The *aurochloride*, $C_4NH_6 \cdot CH_2Ph,HAuCl_4$, crystallises in yellow needles melting at 111°; it is very freely soluble in water. The behaviour of dihydropyrroline with acetic and benzyl chlorides indicates that several of the atoms of hydrogen may be substituted by organic radicles.

S. B. A. A.

Tertiary Pyrroline Derivatives. By C. W. ZANETTI (*Gazzetta*, **20**, 64—69).—1-*Ethyldiacetylpyrroline*, $C_4NH_2Ac_2Et$, is prepared by heating 1-ethylpyrroline (1 part) with acetic anhydride (10 parts) in a sealed tube for seven hours at 250°. From the product a heavy oil may be extracted, which by rectification can be separated into fractions boiling between 200—285° and 285—310° respectively. On distilling the latter fraction under a pressure of 29 mm., the diacetyl derivative

passes over at 183°. It is a yellowish oil with an odour of bitter almonds, and solidifies after a time into a crystalline mass melting at 58—59°; it is very soluble in alcohol, ether, benzene, and light petroleum, but is less soluble in water. The fraction (200—285°) probably contains a mixture of monacetyl and diacetyl derivatives.

1-*Methylpyrrolketonedicarboxylic acid*, $C_4NH_2MeCO(COOH)_2$. When Ciamician and Silber's 1-methyldiacetylpyrroline (Abstr., 1877, 843) is oxidised with potassium permanganate in an alkaline solution, and the product acidified and extracted with ether, a compound is obtained in yellow crusts, which have a decided acid reaction, dissolve with effervescence in solutions of the alkaline carbonates, turn brown at 100°, and decompose at 165°. It is very soluble in water, alcohol, ether, &c. The acid cannot be obtained sufficiently pure for analysis; the *silver* salt has the composition $C_8H_5AgNO_5$. By neutralising the acid with ammonia, an aqueous solution of the ammonium salt is obtained from which salts of iron, copper, lead, &c., may be prepared. A *methyl* salt is obtained by heating the silver salt with methyl iodide. When pure, it crystallises from boiling water in small, white needles which melt at 133—136°, and turn red when exposed to the air. No bromine derivative of either the acid or the methyl salt has hitherto been isolated. S. B. A. A.

Betaïnes of Pyridine Bases. By M. Krüger (*Ber.*, **23**, 2608—2610).—Chloracetic acid combines with pyridine, β-picoline, and ethylpiperidine at 100°, yielding the corresponding betaïne hydrochloride; ethyl chloracetate combines with the above-named bases at the ordinary temperature, the chlorides of the betaïne ethyl salts being formed.

The hydrochlorides of the betaïnes are hygroscopic, crystallise well, and are readily soluble in hot alcohol, but insoluble in ether; the chlorides of the ethyl salts are also very hygroscopic. Both classes of compounds form platinochlorides, &c., and are converted into the betaïnes by moist silver oxide; the free betaïnes readily lose 1 mol. H_2O, yielding the inner anhydrides.

Pyridinebetaïne, $C_7H_7NO_2 + H_2O$, forms a crystalline hydrobromide, nitrate, sulphate, and picrate, as well as a basic hydrochloride of the composition $2C_7H_7NO_2,HCl + H_2O$; with chromic acid, it yields the compound $C_7H_7NO_2,CrO_3$, and with silver nitrate, the compound $C_7H_7NO_2,AgNO_3$. It combines with potassium bismuthoiodide to form a bright-red, crystalline salt of the composition $C_7H_7NO_2,HBiI_4 + 2H_2O$, and when heated with bromine at 100°, it yields pyridinebetaïne hydrobromide. When oxidised with potassium permanganate and when distilled, it is converted into pyridine, but on reduction with sodium amalgam, it yields a base, the platinochloride of which has probably the composition $(C_7H_{11}NO)_2,H_2PtCl_6$. F. S. K.

Action of Methyl Iodide on Pentamethyldihydropyridine. By F. Anderlini (*Gazzetta*, **20**, 61—64).—Unlike most tertiary bases which combine with 1 mol. of methyl iodide yielding the iodide of a compound ammonium, pentamethyldihydropyridine reacts with 2 mols. of methyl iodide forming the hydriodide of a new base, $C_{12}H_{21}N$.

The hydriodide is obtained in the form of a brown syrup, and cannot be directly analysed; it may be converted into the hydrochloride by decomposing its aqueous solution with silver chloride; the hydrochloride gives no precipitate with platinic chloride, but it yields an oily *picrate* and an *aurochloride*, $C_{12}H_{21}N,HAuCl_4$, which crystallises in needles and melts at 99·5—100·5°. On treating the aqueous solution of the hydriodide with caustic potash and steam-distilling the oily product, an easily oxidisable oil with a penetrating odour passes over; this yields a deliquescent uncrystallisable hydrochloride, from which an oily picrate and an aurochloride identical with that described may be obtained. If the new base is in reality a pyridine derivative, as appears probable, it would necessarily have the constitution of a *heptamethyldihydropyridine*. S. B. A. A.

The Second β-Picoline, and the Constitution of Pyridine and Benzene. By A. LADENBURG (*Ber.*, **23**, 2688—2693).—It has previously been pointed out (*Ber.*, **23**, 1010) that the β-picoline obtained by Hesekiel from glycerol differs in certain particulars from that obtained by Stöhr from strychnine, and the author has therefore re-examined the compounds from both sources with great care, and finds that they are in fact not identical. The base obtained from strychnine is termed β′-picoline in the sequel.

In agreement with previous determinations, the boiling point of β-picoline was found to be 141·5—142° (uncorr.), and β′-picoline 146—149·5° (uncorr.), and the melting points of the mercury double salts to be 145—146° and 139—140° respectively.

There is also a very marked difference in their behaviour when mixed with water. When the latter is added drop by drop to β-picoline, no cloudiness is observed under any conditions; with β′-picoline, however, a separation of an oily layer soon takes place, which disappears on shaking so long as the quantity of water is small and the temperature low. A mixture of 1 vol. of the base with 3 vols. of water is most susceptible to slight changes of temperature, the warmth of the hand being sufficient to cause an immediate precipitation, and in the summer the liquid separates completely into two distinct layers. Moreover, the platinochlorides of both bases readily pass into the corresponding platinous chlorides on boiling with water, which are also not identical with one another, the β-picoline salt melting at 240—241°, and that of β′-picoline at 256—258°.

There can therefore be no doubt that two isomeric β-picolines exist, and it is also probable that the same is true of nicotinic acid, α-picoline, and α-picolinic acid. As regards α-picoline, it may be mentioned that the compound obtained by Weidel from bone oil (Abstr., 1880, 268) differs in certain respects from that obtained synthetically by Ladenburg and Lange (*Annalen*, **247**, 6). If this difference is confirmed, the existence of five isomeric monosubstituted picolines will have been proved, which in turn will be a final proof of the Körner-Dewar formula of pyridine.

The author also believes that the existence of two isomeric β-picolines of this constitution shows that Kekulé's formula really demands the existence of five isomeric disubstitution products of benzene, and

that the prism formula is the only one which satisfies the laws of subtitution. This formula does not, however, account for all the relationships of benzene, and it will therefore be necessary to retain the hexagonal formula along with the prism formula. H. G. C.

Formation of Lepidine Derivatives from Chinine and Cinchine. By W. Koenigs (*Ber.*, **23**, 2669—2679).—When chinine, obtained by Comstock and Koenigs from quinine (Abstr., 1887, 281, 1122), is allowed to remain for 14 days with hydrobromic acid, saturated at $-17°$, 1 mol. of methyl bromide is formed, and *hydrobromoxycinchine hydrobromide*, $C_{19}H_{21}BrN_2O,2HBr$, separates out. The free base is obtained by the action of ammonium carbonate, and purified by recrystallisation from alcohol. It is sparingly soluble in alcohol, but dissolves more readily in chloroform, and melts indefinitely at 180—190°. Its *sulphate* crystallises in slender, yellow, concentrically grouped needles. When boiled with alcoholic potash, it is converted into the corresponding *oxycinchine*, $C_{19}H_{20}N_2O$, which is purified by conversion into the tartrate, the latter being sparingly soluble in cold water. Oxycinchine is a yellowish, amorphous compound which melts at 100—110°, is readily soluble in methyl and ethyl alcohol, acetone, and chloroform, but could not be obtained crystalline. The salts are for the most part readily soluble, and the *hydrochloride* may be crystallised from absolute alcohol. The *platinochloride*, $C_{19}H_{20}N_2O,H_2PtCl_6$, crystallises from hot, dilute hydrochloric acid in yellow, sparingly soluble plates.

On continued boiling with concentrated hydrobromic acid, oxycinchene, like chinine, is converted into apocinchene, $C_{19}H_{19}NO_2$. If, however, it be heated with ammonio-zinc chloride and ammonium chloride, in the manner described by Merz and Müller (Abstr., 1887, 243), a totally different reaction takes place, *paramidolepidine*, $C_9NH_5Me{\cdot}NH_2$, being formed. This is separated from the product of the reaction by extraction with water and dilute soda solution, which is in turn extracted with ether. The crude base remaining on evaporation is purified by conversion into the crystalline acid tartrate, decomposing the latter with sodium carbonate, and crystallising from hot water. Paramidolepidine is thus obtained in beautiful, colourless needles which melt at 168—170°, and are readily soluble in alcohol and chloroform, but somewhat more sparingly in ether and hot water. It dissolves in dilute mineral acids with a yellow colour, which disappears with an excess of acid, the solutions showing a green fluorescence. When treated with sodium nitrite and an alkaline solution of stannous chloride, it yields a compound corresponding in its properties to lepidine.

When the zinc soluble salt of chinine (Abstr., 1887, 281) is heated with water at 190—200° under pressure, it yields, besides resinous matters, *paramethoxylepidine*, $C_9NH_5Me{\cdot}OMe$, which is purified by successive conversion into the acid tartrate and the sulphate. The free base, obtained from the latter by treatment with alkalis, crystallises from dilute alcohol in slender, colourless needles, and melts at 50—51°. It gives the quinine reaction with chlorine-water and ammonia, the coloration being, however, of a greenish-blue tint, and

the solution, if not too dilute, yields after a time a precipitate resembling Prussian blue. The *zincochloride* crystallises in small, colourless needles melting at 245° with decomposition, and the *platinochloride*, $(C_{11}H_{11}NO)_2,H_2PtCl_6$, forms an orange-yellow, crystalline powder, very sparingly soluble in hot water, and melting at 236—237° with decomposition. In addition to paramethoxylepidine, a compound is also formed in the above reaction which appears to be identical with the parahydroxylepidine described below. Paramethoxylepidine is among the products of the action of potash on quinine and the allied alkaloïds (compare Krakau, Abstr., 1885, 1081).

Parahydroxylepidine, $C_9NH_5Me{\cdot}OH$, is obtained by heating paramethoxylepidine with concentrated hydrobromic acid. The diluted acid solution is treated with an excess of sodium carbonate, the precipitate dissolved in caustic soda solution, reprecipitated by carbonic anhydride, and crystallised from 50 per cent. alcohol. It forms colourless needles which melt and become brown at 216—218°, and are sparingly soluble in hot water; the solution does not give any characteristic colour reaction with ferric chloride. The *hydrogen tartrate* also crystallises well.

When cinchene is heated with water and acetic acid at 200° for 10 hours, it behaves in a similar manner to chinine, and is converted into lepidine. Quinine and cinchonine, on the other hand, under the same conditions only yield traces of methoxylepidine or lepidine, whilst benzylidinelepidine, $C_9NH_6{\cdot}CH{:}CHPh$, is readily split up into lepidine and benzaldehyde. It is possible therefore that in chinine and cinchene, the carbon atoms next to the quinoline ring are also doubly linked, and that in quinine and cinchonine a hydrogen atom and a hydroxyl group are combined with these atoms. This is not, however, sufficient by itself to explain the formation of apochinine and apocinchene (*loc. cit.*), or to explain the fact that the latter are so much more stable than the compounds from which they are obtained.

H. G. C.

Substitution Products of Lepidine. By A. Busch and W. Koenigs (*Ber.*, **23**, 2679—2688).—In view of the results mentioned in the previous abstract, it appeared desirable to obtain para-derivatives of lepidine directly from the base itself. From the results of Weidel (Abstr., 1882, 225) and Georgievics (Abstr., 1888, 501), it appeared most probable that such compounds would be obtained by the sulphonation of lepidine at a high temperature, and it was found that the parasulphonic acid can in fact be thus readily prepared. In carrying out the reaction, lepidine (2 grams) is mixed with eight times the quantity of pure sulphuric acid, cooling during the addition, and then heated for half an hour at 300°, and poured, on cooling, into 10—15 times the volume of absolute alcohol. The separated sulphonic acid crystallises from hot water in almost colourless, silky needles, having the composition $C_9NH_5Me{\cdot}SO_3H + H_2O$, the water of crystallisation being given off at 100°. The *silver* salt crystallises in slender, colourless needles, also containing 1 mol. of water of crystallisation, which is given off at 140°, the residue assuming a reddish coloration; the *mercuric* salt is a crystalline precipitate. The

acid is quite different from the lepidinesulphonic acid described by Weidel and Hazura (Abstr., 1885, 562).

As the parasulphonic acid is only slightly attacked by chromic acid, it was first converted into the *benzylidene* compound,

$$SO_3H\cdot C_9NH_5\cdot CH:CHPh,$$

by heating with benzaldehyde, zinc chloride, and a little water. This forms sulphur-yellow crystals containing 2 mols. of water of crystallisation, which are given off at 180°, the sulphur-yellow colour changing to orange. To carry out the oxidation, this compound is dissolved in the requisite quantity of soda solution, and a 1 per cent. solution of potassium permanganate added, until it is no longer decolorised on standing. The solution is then boiled, decolorised with a little sodium hydrogen sulphite, filtered, and acidified with nitric acid. The crystals which separate on cooling are extracted with alcohol and ether to remove benzoic acid, and recrystallised from water. *Sulphocinchonic acid*, $C_{10}H_7NSO_5 + H_2O$, is thus obtained in fascicular aggregates of lustrous, colourless needles, containing 1 mol. H_2O. It dissolves readily in hot, less easily in cold water, and still less in alcohol, and bears the strongest resemblance to the β-sulphocinchonic acid obtained by Weidel and Georgievics (*loc. cit.*) from α-cinchonic acid. On fusion with potash, it yields a β-hydroxycinchonic acid identical with Skraup's xanthochinic acid, and is therefore probably a para-compound. This assumption is also supported by the fact that quinoline, by sulphonation under similar circumstances, yields an undoubted para-derivative. The acid obtained by Weidel differed from the acid from benzylidinelepidinesulphonic acid, inasmuch as it contained 2 mols. H_2O; but cinchonic acid itself crystallises sometimes with 1 mol. and sometimes with 2 mols. H_2O.

Parahydroxylepidine, $C_9NH_5Me\cdot OH$, is obtained from the sulphonic acid by fusion with soda and a little water in the usual manner. It crystallises from hot water, after treatment with animal charcoal, in colourless, fascicular aggregates of needles melting and becoming brown at 216—218°, and identical with the compound obtained from chinine (see preceding abstract). The corresponding *paramidolepidine*, $C_9NH_5Me\cdot NH_2$, prepared from the hydroxy-compound by heating it with ammonio-zinc chloride, is also identical with the compound there described.

When lepidine and sulphuric acid are mixed without cooling, and slowly heated to 300°, a sulphonic acid is obtained which appears to consist of a mixture of the above lepidineparasulphonic acid with an isomeric acid, probably the ortho-compound. When the mixture is fused with 6 parts of potash and 6 parts of soda, the melt acidified with sulphuric acid, made slightly alkaline, and distilled in a current of steam, it yields a greenish, crystalline compound with a peculiar odour melting at 141°. It probably consists of *orthohydroxylepidine*, and yields a *platinochloride*, $(C_{10}H_9NO)_2,H_2PtCl_6$, crystallising in orange-yellow needles.

Ortho- (?) nitrolepidine is prepared by mixing 1 part of lepidine with 1 part of sulphuric acid, and adding, first, 5 parts of colourless

fuming nitric acid of sp. gr. 1·525, and then 5 parts of sulphuric acid, and allowing the mixture to remain for 12 hours; the liquid is then poured into water, soda added, and the solution extracted with benzene. The oily residue obtained on evaporating the latter is treated with light petroleum, and the brown crystals thus formed repeatedly crystallised from absolute alcohol. It forms lustrous, almost colourless needles melting at 126—127°, and sparingly soluble in cold alcohol. Nitroquinoline is best prepared in a similar manner from quinoline.

H. G. C.

α-Picolylethylalkine and its Derivatives. By A. MATZDORFF (*Ber.*, **23**, 2709—2713).—α-Picoline and propaldehyde unite together in presence of water when heated at 160—170° under pressure, forming *α-picolylethylalkine*, $C_5NH_4·CH_2·CHEt·OH$. The product is made alkaline, distilled in a current of steam, acidified, and extracted with chloroform, again made alkaline, and re-extracted with chloroform. The second extract leaves the α-picolylethylalkine on evaporation as a reddish-brown oil, which is purified by distillation in a vacuum. It forms a colourless oil which boils at 125—127° (18 mm.), is readily soluble in water, alcohol, and chloroform, and becomes yellow in the air. It can only be dried by means of potassium carbonate, as water is readily split off if potassium hydroxide is used. The *platinochloride*, $(C_9H_{13}NO)_2,H_2PtCl_6$, forms cubical crystals which melt at 154° with decomposition, and the *aurochloride*, $C_9H_{13}NO,HAuCl_4$, crystallises in long needles melting at 97·5—99°.

As mentioned above, α-picolylethylalkine loses water in contact with potash, the product formed being 2-crotylpyridine. In this manner it is, however, always obtained mixed with α-picoline, and it is better to prepare it by heating the alkine with concentrated hydrochloric acid at 160—170°, saturating with soda, and distilling in a current of steam. *Crotylpyridine*, $C_5NH_4·CH{:}CHEt$, is a colourless, mobile liquid having a strong conyrine-like odour; it boils at 147—149° (75 mm.), and is readily soluble in alcohol, ether, and chloroform, but almost insoluble in water. Its *platinochloride*, $(C_9H_{11}N)_2,H_2PtCl_6$, crystallises in beautiful needles or plates melting at 140°, and its *aurochloride*, $C_9H_{11}N,HAuCl_4$, in small needles which blacken and melt at 127·5—130°.

On reduction with sodium in alcoholic solution, α-picolylethylalkine readily yields the corresponding *α-pipecolylethylalkine*,

$$C_5NH_{10}·CH_2·CHEt·OH,$$

an almost colourless oil boiling at 242—243°, and readily soluble in water, alcohol, and ether. It does not yield salts. H. G. C.

Methylethylpyridylalkine. By G. PRAUSNITZ (*Ber.*, **23**, 2725—2726).—The collidine, C_5NH_3MeEt, prepared by heating aldehyde-ammonia with paraldehyde, was heated with formaldehyde and a 1½ per cent. soda solution in sealed tubes for 10—12 hours at 160—170°. The contents were then washed out with water and distilled with steam, and the *methylethylpyridylalkine*,

$$C_5NH_3Et·CH_2·CH_2·OH,$$

extracted from the residue with chloroform. It is a pale yellow oil of sp. gr. 1·066 at 0°, and boils at 147—149° under 18 mm. pressure. It dissolves easily in water and alcohol, less easily in ether. The *platinochloride*, $2C_9H_{13}NO,H_2PtCl_6$, forms red, cubical crystals which melt at 159° with effervescence. The *aurochloride* forms brilliant, yellow plates, the *picrate* small, very soluble prisms. The cadmio-iodide is an oil. C. F. B.

α-Picolylfurylalkine and α-Pipecolylfurylalkine. By O. KLEIN (*Ber.*, **23**, 2693—2696).—Furfuraldehyde combines with α-picoline when mixed with a little water and heated at 140—150° under pressure for 8—9 hours, no elimination of water taking place. The product is distilled in a current of steam to remove hydrocarbons and unaltered α-picoline and furfuraldehyde, the residue extracted with chloroform and, after evaporation of the latter, distilled under diminished pressure. The base passes over at 164° under 20 mm. pressure as a greenish liquid, which solidifies to a hard yellow cake. On analysis it gave numbers agreeing with the formula $C_{11}H_{11}NO_2$, and it is therefore *α-picolylfurylalkine*, $C_5NH_4{\cdot}CH_2{\cdot}CH(OH){\cdot}C_4OH_3$. It has a characteristic, not unpleasant, odour, and is readily soluble in alcohol, ether, and chloroform, insoluble in water, and melts at 41—43°. Its *platinochloride*, $(C_{11}H_{11}NO_2)_2,H_2PtCl_6$, forms brownish-yellow, fascicular aggregates of crystals melting at 160—162° with decomposition; the *mercurochloride*, $C_{11}H_{11}NO_2,HHgCl_3$, crystallises in beautiful, iridescent needles melting at 147—150°, the *cadmio-iodide*, $C_{11}H_{11}NO_2,HCdI_3$, in yellowish-red plates, and the *picrate*, $C_{11}H_{11}NO_2,C_6H_3N_3O_7$, in yellow needles melting at 157—160°.

When α-picolylfurylalkine is treated with benzoic anhydride, it forms *benzoylpicolylfurylalkeïne*, $C_{11}H_{10}BzNO_2$, which crystallises in brown, fascicular aggregates and melts at 47—49°. Its *platinochloride*, $(C_{11}H_{10}BzNO_2)_2,H_2PtCl_6$, forms small, brown needles melting at 140—145° with decomposition, and its *mercurochloride*,

$$C_{11}H_{10}BzNO_2,HHgCl_3,$$

crystallises from dilute hydrochloric acid in pale yellow needles. The corresponding *acetyl* derivative, $C_{11}H_{10}AcNO_2$, could only be obtained as a dark brown oil, but its *platinochloride*, $(C_{11}H_{10}AcNO_2)_2,H_2PtCl_6$, crystallises from water containing hydrochloric acid in brownish needles melting at 163—165°, and its *mercurochloride*,

$$C_{11}H_{10}AcNO_2,HHgCl_3,$$

in small, yellow needles melting at 152—155° with decomposition.

On reduction with sodium in alcoholic solution, α-picolylfurylalkine is converted into the corresponding hydro-base, *α-pipecolylfurylalkine*. This is a yellowish oil boiling at 248—251° (760 mm.), and 118—123° (15 mm.). It gradually becomes of a darker colour, and does not yield crystalline salts. H. G. C.

Metanitro-α-stilbazole, its Reduction Products, and Anisilidenepyridylalkine. By A. SCHUFTAN (*Ber.*, **23**, 2716—2719).—Metanitrobenzaldehyde was treated with picoline, the mixture acidi-

fied, diluted with water, extracted with ether, and finally decomposed with potash. *Metanitro-α-stilbazole*, $NO_2\cdot C_6H_4\cdot CH:CH\cdot C_5NH_4$, then separated in brown flakes which, when purified with animal charcoal and recrystallised from alcohol, formed shining, white plates melting at 120°, dissolving easily in alcohol, ether, chloroform, and carbon bisulphide, sparingly in hot, and not at all in cold water; its solution is neutral. The *platinochloride*, $2C_{13}H_{10}N_2O_2,H_2PtCl_6$, forms yellow needles melting with decomposition at 240°. The *mercurochloride*, $C_{13}H_{10}N_2O_2,HHgCl_3$, crystallises in groups of yellowish needles melting at 211° with decomposition. The *picrate* forms brilliant, golden-yellow plates which blacken when heated. The substance also yields a bromine additive product which crystallises from alcohol in white needles melting at 145°.

When the nitro-compound is reduced with tin and hydrochloric acid, it yields *metamido-α-stilbazole*, $NH_2\cdot C_6H_4\cdot CH:CH\cdot C_5NH_4$, which crystallises from dilute alcohol in yellowish needles melting at 85°, and when dried in a vacuum has the composition $C_{13}H_{12}N_2,\frac{1}{2}H_2O$. It is a di-acid base with an alkaline reaction, and dissolves sparingly in water, easily in alcohol, ether, and chloroform. The *platinochloride*, $2C_{13}H_{12}N_2,H_2PtCl_6,H_2O$, forms groups of very soluble, reddish-yellow needles which blacken when heated. The *mercurochloride* forms groups of white needles very soluble in water. A bromine additive product was also obtained.

When the original nitro-compound is reduced with sodium and absolute alcohol, *metamido-α-stilbazoline*, $NH_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot C_5NH_{10}$, is obtained as a strongly alkaline, yellow oil boiling above 360° under atmospheric pressure, and at 200—205° under 25 mm. It smells like piperidine, gives the nitroso-reaction for the imido-group, and dissolves in alcohol, ether, chloroform, and hot water. Its *platinochloride* forms very unstable, yellow plates. No other crystalline salts could be obtained.

By treating picoline with anisaldehyde, *anisilidenepyridylalkine*, $OMe\cdot C_6H_4\cdot CH:CH\cdot C_5NH_4$, was obtained in brilliant, white, cetaceous plates, melting at 97°, soluble in ether and chloroform, and sparingly in hot water.

The *platinochloride*, $2C_{14}H_{13}NO,H_2PtCl_6$, forms yellow plates melting at 184°. C. F. B.

Hydroxy-α-stilbazole and its Derivatives. By F. BUTTER (*Ber.*, **23**, 2697—2700).—When α-picoline (10 grams), salicylaldehyde (13 grams), and water (7 grams) are heated in a sealed tube at 140°, the first two compounds unite together directly. The product is treated with hydrochloric acid, extracted with ether, made alkaline, and distilled in a current of steam. The residue on cooling deposits the crude base as a brown, solid mass, which is recrystallised from dilute alcohol and finally from water. It is thus obtained as an almost white, crystalline compound sparingly soluble even in hot water, readily in alcohol and ether. Analysis confirmed the formula $C_{13}H_{11}NO$, and it is therefore from its mode of formation *hydroxy-α-stilbazole*, $C_5NH_4\cdot CH:CH\cdot C_6H_4\cdot OH$. It is neutral towards litmus, but dissolves in acids and also in soda. Its *platinochloride*,

$(C_{13}H_{11}NO)_2, H_2PtCl_6$, forms dull, reddish-brown needles which melt at 187—188° with decomposition, and its *mercurochloride* forms radial, eccentric groups of needles melting at 167—170°.

When hydroxy-α-stilbazole (3 grams) is treated with soda (0·7 gram) and ethyl iodide (2·3 grams) in aqueous solution, it is converted into *ethoxy-α-stilbazole*, $C_5NH_4·CH:CH·C_6H_4·OEt$. This is a yellow, non-crystallisable oil, which yields a *platinochloride*, $(C_{15}H_{15}NO)_2,H_2PtCl_6$, as a reddish-yellow, crystalline powder melting at 181—183°, and a *mercurochloride*, $(C_{15}H_{15}NO)_2,HHgCl_3$, crystallising in pale yellow needles which melt at 91—92°. If double the quantity of ethyl iodide given above be taken, *ethoxy-α-stilbazole ethiodide* $C_5NH_4·CH:CH·C_6H_4·OEt,EtI$, is formed, and crystallises from hot dilute alcohol in golden-yellow, transparent crystals melting at 217·5°.

Hydroxy-α-stilbazole is acted on by bromine-water in hydrochloric acid solution, the *dibromide*, $C_5NH_4·CHBr·CHBr·C_6H_4·OH$, being formed as an oil which solidifies to yellow, crystalline flocks. On reduction with sodium in alcoholic solution, hydroxy-α-stilbazole is converted into *hydroxy-α-stilbazoline*, $C_5NH_{10}·CH_2·CH_2·C_6H_4·OH$, crystallising from light petroleum in white, arborescent aggregates of crystals which melt at 93—94°, and do not yield crystalline salts.

H. G. C.

Derivatives of β-Pyrazole. By MAQUENNE (*Compt. rend.*, **111**, 113—116).—An aqueous solution of nitrotartaric acid is mixed with a corresponding quantity of aldehyde and an excess of ammonia. Heat is developed, and after some time a crystalline mass of ammonium β-pyrazole-4 : 5-dicarboxylate separates. The free acid is obtained by saturating the cold ammoniacal liquid with hydrochloric acid; nitrogen oxides are evolved, and hence nitrotartaric acid has behaved towards the alkali as if it were the symmetrical dinitrous ether of dihydroxytartaric acid. If a mixture of sodium dihydroxytartrate and aldehyde is boiled with excess of ammonia, the slightly soluble sodium salt of the same pyrazolecarboxylic acid separates, and hence it is clear that in the reaction first mentioned the nitrotartaric acid is first converted into dihydroxytartaric acid and ammonium nitrite.

β-Pyrazole-4 : 5-dicarboxylic acid (glyoxalinedicarboxylic acid), $C_3N_2H_2(COOH)_2$, is obtained from formaldehyde in ammoniacal solution, and forms a white powder consisting of slender needles or microscopic octahedra. It is almost insoluble in water, and its salts with the alkalis and alkaline earths, although crystallisable, are only slightly soluble. The other salts are generally amorphous; only the mono-metallic salts are well-defined. Dry distillation converts the acid completely into β-pyrazole (glyoxaline).

2-Methyl-β-pyrazole-4 : 5-dicarboxylic acid, $C_3N_2HMe(COOH)_2 + H_2O$, is obtained easily from ordinary aldehyde. It is only slightly soluble, even in boiling water, but crystallises in brilliant, white needles, which begin to lose water at about 130°, but only become anhydrous at 170°. The mono-metallic salts of the alkalis and alkaline earths are only slightly soluble, but crystallise readily in

anhydrous crystals. When heated, the acid yields glyoxalethyline and carbonic anhydride.

Isobutylglyoxalinedicarboxylic acid and *phenylglyoxalinedicarboxylic acid* are obtained in a similar manner, and the reaction seems to be general for primary aldehydes of simple function. Although the constitution of these acids shows that they should be bibasic, they form only mono-metallic salts. At the same time, the acids form neither hydrochlorides nor platinochlorides, and hence it would seem that the strongly basic pyrazole nucleus saturates one of the acid functions.

C. H. B.

Constitution of Carbizines. By M. FREUND and F. KUH (*Ber.*, **23**, 2821—2844).—Freund and Goldsmith have described (Abstr., 1888, 1187) a series of compounds, prepared by the action of carbonyl chloride on acid derivatives of phenylhydrazine, which they regarded as derivatives of the hypothetical carbizine group $CO<\begin{smallmatrix}NH\\|\\NH\end{smallmatrix}$. The corresponding sulphur compounds, prepared by E. Fischer and Besthorn (compare Abstr., 1888, 1091), by heating phenylthiosemicarbazide, were believed to have the formula $NPh<\begin{smallmatrix}N\\||\\C\cdot SH\end{smallmatrix}$, since they are isomeric with the substances obtained by the action of thiocarbonyl chloride on acid phenylhydrazine derivatives. It is found, however, that diphenylcarbazide only reacts with 1 mol. of carbonyl chloride or thiocarbonyl chloride, instead of 2 mols. as would be expected from the constitution of the carbizines. Only one of the oxygen atoms of acetylphenylcarbazide reacts with phosphorus pentachloride. Contrary to expectation, carbonyl chloride has no action on certain compounds, the atoms of which are not linked in a ring. These results all point to the conclusion that acid derivatives of phenylhydrazine are tautomeric, and have the two forms

$$NHPh\cdot NH\cdot CO\cdot R \text{ and } NHPh\cdot N\colon CR\cdot OH;$$

the compounds obtained by the action of carbonyl chloride and thiocarbonyl chloride are derived from the second form, and consequently contain the complex $\begin{smallmatrix}NH\cdot N\\|\\ [S]\,CO\cdot O\end{smallmatrix}\!\!>CR$. It is proposed to term the groups $O<\begin{smallmatrix}CH_2\cdot NH\\|\\CH\colon N\end{smallmatrix}$ and $O<\begin{smallmatrix}CO\cdot NH\\|\\CH\colon N\end{smallmatrix}$ biazoline and biazolone respectively; the corresponding sulphur compounds,

$$S<\begin{smallmatrix}CO\cdot NH\\|\\CH\colon N\end{smallmatrix},\ O<\begin{smallmatrix}CS\cdot NH\\|\\CH\colon N\end{smallmatrix},\ \text{and}\ S<\begin{smallmatrix}CS\cdot NH\\|\\CH\colon N\end{smallmatrix},$$

being called thiobiazolone, ψ-thiobiazolone, and dithiobiazolone.

Phenylazophenylthiobiazolone, $\begin{smallmatrix}NPh\cdot N\\|\\CO-S\end{smallmatrix}\!\!>C\cdot N_2Ph$, is prepared by the action of carbonyl chloride on diphenylthiocarbazide; it crystallises from alcohol in stellate groups of golden needles melting at 140°, and is insoluble in water, but readily dissolves in ether, benzene, or chloroform. This compound is derived, in all probability, from the tauto-

merie form of the carbazide $NHPh\cdot N{:}C(SH)\cdot NH\cdot NHPh$; it may also be obtained by the action of carbonyl chloride on the blue dye $NPh{:}N\cdot CS\cdot NH\cdot NHPh$, which is formed by the oxidation of diphenylthiocarbazide.

Phenylhydrazophenylthiobiazolone, $\begin{array}{l}NPh\cdot N\\ |\\ CO-S\end{array}\!\!>C\cdot NH\cdot NHPh$, is obtained by the reduction of the previous compound with hydrogen sulphide; it crystallises from alcohol in small, white, interlaced needles melting at 124°, and is more readily soluble in ether or alcohol than the azo-derivative. By the action of oxidising agents, or of carbonyl chloride, the azo-compound is regenerated. Experiments with thiocarbonyl chloride on diphenylsulphocarbazide were unsuccessful.

Phenylazophenyldithiobiazolone, $\begin{array}{l}NPh\cdot N\\ |\\ CS-S\end{array}\!\!>C\cdot N_2Ph$, is prepared by the action of thiocarbonyl chloride on the above blue compound; it is deposited from benzene in dark-red crystals which melt at 160—165° with partial decomposition, and are readily soluble in alcohol, ether, chloroform, and glacial acetic acid, but more sparingly in benzene or light petroleum. On reduction with hydrogen sulphide, *phenylhydrazophenyldithiobiazolone*, $\begin{array}{l}NPh\cdot N\\ |\\ CS-S\end{array}\!\!>C\cdot NH\cdot NHPh$, is formed, crystallising in brown plates which melt at 142°, and are sparingly soluble in alcohol, but more readily in ether, benzene, or light petroleum.

Phenylhydrazophenylbiazolone, $\begin{array}{l}NPh\cdot N\\ |\\ CO-O\end{array}\!\!>C\cdot NH\cdot NHPh$, is prepared by heating diphenylcarbazide with carbonyl chloride in a sealed tube at 160°; it is deposited from alcohol or glacial acetic acid in white crystals which melt at 180—181°, and are insoluble in benzene and toluene, but soluble in ether or chloroform. On oxidation with ferric chloride, *phenylazophenylbiazolone*, $\begin{array}{l}NPh\cdot N\\ |\\ CO-O\end{array}\!\!>C\cdot N_2Ph$, is formed, crystallising from alcohol in small, yellow plates melting at 198—200°. By the action of tin and hydrochloric acid on phenylhydrazophenylbiazolone, aniline is eliminated, and *phenylamidobiazolone* (*amidophenylcarbizincarboxylic acid*), $\begin{array}{l}NPh\cdot N\\ |\\ CO-O\end{array}\!\!>C\cdot NH_2$, is formed.

Phenylazophenyl-ψ-thiobiazolone, $\begin{array}{l}NPh\cdot N\\ |\\ CS-O\end{array}\!\!>C\cdot N_2Ph$, is prepared by the action of thiocarbonyl chloride on diphenylcarbazine at 150°; it is deposited from glacial acetic acid in clusters of yellowish-red crystals melting at 170° with partial decomposition, and is readily soluble in all the ordinary media except water.

Phenylmethyldichlorobiazolone, $\begin{array}{l}NPh\cdot N\\ |\\ CCl_2\cdot O\end{array}\!\!>CMe$, is prepared by heating a mixture of phosphorus pentachloride and phenylmethylbiazolone (acetylphenylcarbizine) in molecular proportion at 150°; it crystallises from anhydrous ether in stellate groups of small, white needles which melt at 120—122°, and are readily soluble in benzene, chloroform, or

light petroleum. The compound is slowly decomposed by water at ordinary temperatures, the biazolone being regenerated. Phenylmethyl-ψ-thiobiazolone is formed by the action of hydrogen sulphide on the dichloride; it has been previously prepared by treating acetylphenylhydrazine with thiocarbonyl chloride. All attempts to prepare phenylmethyltetrachlorobiazolone were fruitless. Phenylthiocarbamide is formed by the action of phosphorus pentasulphide on phenylmethylbiazolone.

Phenylmethylimidobiazole, $CMe\lessdot\begin{matrix}N\cdot NPh\\ \quad\vert\\ O\cdot C:NH\end{matrix}$, is obtained by heating the chlorinated derivative with alcoholic ammonia in a sealed tube for 3—4 hours at 150°; it crystallises from alcohol in small, white needles melting at 112°, and is readily soluble in ether, benzene, or light petroleum; the biazolone is regenerated on treatment with water. The compound could not be obtained by the direct action of ammonia on the biazolone. *Phenylmethylbiazoline*, $\begin{matrix}NPh\cdot N\\ \vert\quad\\ CH_2\cdot O\end{matrix}\gtrdot CMe$, prepared by the reduction of the chloro-compound with zinc and hydrochloric acid, after repeated recrystallisations from alcohol, is deposited in slightly yellow plates melting at 140°.

Paradichlorohydrazobenzene may readily be obtained from paradichlorazobenzene by reduction in alcoholic solution; no derivative of carbonyl chloride could be prepared, the compound being either recovered unaltered, or else completely decomposed, according to the experimental conditions. Similar results were observed with hydrazotoluene, and also with the three compounds obtained by Fries by the action of phenylhydrazine on cyanuric chloride. J. B. T.

Quinazolines. By S. GABRIEL and R. JANSEN (*Ber.*, **23**, 2807—2814).—*Orthonitrobenzylbenzamide*, $NO_2\cdot C_6H_4\cdot CH_2\cdot NHBz$, is prepared by treating an aqueous solution of orthonitrobenzylamine hydrochloride (1 mol.) with sodium hydroxide (2 mols.) and benzene chloride (1 mol.); after some time, the oil which forms solidifies, and on recrystallisation from alcohol the compound is deposited in colourless needles melting at 110—112°. *Orthoamidobenzylbenzamide*, $NH_2\cdot C_6H_4\cdot CH_2\cdot NHBz$, is formed by the reduction of the nitro-compound with alcoholic hydrochloric acid and zinc; the product is treated with excess of sodium hydroxide, and extracted with ether; the residue remaining after evaporation of the ether crystallises from benzene in needles which melt at 108—109° (180—190°?). It is readily soluble in ether, alcohol, chloroform, and dilute acids. On distillation, it yields benzonitrile, orthotoluidine, water, and *phenylquinazoline*, $C_6H_4<\begin{matrix}CH:N\\ N:CPh\end{matrix}>$, which boils above 300°, and crystallises from methyl alcohol in yellow, rhombic needles melting at 100—101°; it is a feeble base, and yields a colourless, crystalline *hydrochloride*.

Orthoamidobenzylacetamide, $NH_2\cdot C_6H_4\cdot CH_2\cdot NHAc$, is prepared from orthonitrobenzylacetamide by reduction with zinc and hydrochloric acid; it is readily soluble in ordinary menstrua, and crystallises from water in long needles melting at 112·5—113·5°. The *platinochloride*

is crystalline. On distillation, water is eliminated, and above 300° *β methyldihydroquinazoline*, $C_6H_4<\begin{matrix}CH_2\cdot NH\\ N=CMe\end{matrix}$, passes over as a yellow, viscid liquid, which becomes colourless on purification; it is bitter to the taste, and the aqueous solution has an alkaline reaction. The *hydrochloride*, crystallises from methyl alcohol in short, colourless prisms which remain solid at 250°. The *picrate* is deposited from water in long needles which soften at about 180° and melt at 200°. The *dichromate* forms slender, reddish-yellow needles. The *platinochloride* is obtained in yellow needles.

Orthonitrobenzylformamide, $NO_2\cdot C_6H_4\cdot CH_2\cdot NH\cdot CHO$, is prepared by boiling orthonitrobenzylamine hydrochloride with anhydrous sodium formate and glacial formic acid for 1½ hours in a reflux apparatus; after treatment with water, the compound is deposited in compact aggregates of colourless, lustrous crystals melting at 88—90°. On reduction with zinc and hydrochloric acid, it yields *dihydroquinazoline*, $C_6H_4<\begin{matrix}CH_2\cdot NH\\ N=CH\end{matrix}$, which is a yellow, viscid liquid; its aqueous solution has an alkaline reaction. The *hydrochloride* is deposited from absolute alcohol in small crystals. The *picrate* crystallises from absolute alcohol, and melts at about 215°, with previous softening at 200°. The *dichromate* and *platinochloride* are sparingly soluble, and crystalline.

J. B. T

Dihydroquinazolines. By C. PAAL and F. KRECKE (*Ber.*, **23**, 2634—2641).—It has been shown by Paal and Busch (this vol., p. 71) that the formyl compounds of orthonitrobenzylaniline and of orthonitrobenzyl-ortho- and para-toluidine are converted, on reduction, into derivatives of quinazoline. The authors have, moreover, examined the action of reducing agents on orthonitrobenzylacetanilide, and find that in this case also a quinazoline derivative is readily formed.

Orthonitrobenzylacetanilide, $NO_2\cdot C_6H_4\cdot CH_2\cdot NAcPh$, is readily obtained by boiling orthonitrobenzylaniline for 1—2 hours with acetic anhydride (compare Lellman and Stickel, Abstr., 1886, 793). It forms large, transparent, yellowish crystals which melt at 75°, and are insoluble in water, sparingly soluble in light petroleum, but readily in the other common organic solvents. On reduction with tin and hydrochloric acid in alcoholic solution, it yields the stannochloride of *2-methyl-3-phenyldihydroquinazoline*, $C_6H_4<\begin{matrix}N=CMe\\ CH_2\cdot NPh\end{matrix}$, which is converted into the *hydrochloride*, $C_{15}H_{14}N_2,HCl$, by treatment with hydrogen sulphide in dilute alcoholic solution. This forms colourless, transparent crystals containing 2 mols. H_2O, readily soluble in hot water and alcohol, which melt at 256—257°. The *platinochloride*, $C_{15}H_{14}N_2,H_2PtCl_6$, crystallises from hot alcohol in lustrous, flat, orange needles which decompose at 223°. To obtain the free base, the pure hydrochloride is decomposed with alkali, the separated oil extracted with ether, and the ethereal solution dried and evaporated. The residual oil gradually solidifies, and may then be recrystallised from benzene. It forms rosette-shaped groups of

waxy needles which melt at 58—60°, and are insoluble in water, moderately soluble in light petroleum, and readily in other organic solvents and in mineral acids; with the latter it forms stable, well-crystallised salts.

When orthonitrobenzylaniline is reduced with tin and hydrochloric acid, it does not yield the corresponding orthamidobenzylaniline, but a base having the empirical formula $C_{13}H_{10}N_2$. It crystallises from hot alcohol in almost colourless needles melting at 81—83°, insoluble in water, sparingly soluble in light petroleum, readily in concentrated acids and organic solvents, and unlike orthoamidobenzylaniline it does not yield a quinazoline derivative when boiled with formic acid. Its *platinochloride* is a yellow, flocculent precipitate.

The above results agree well with those obtained by Lellmann and Stickel (*loc. cit.*), but not with those of Söderbaum and Widman (this vol., p. 1258). The latter investigators state that orthonitrobenzyltoluidine and orthonitrobenzanilide, on reduction, simply pass into the corresponding amido-compounds; and do not, as Lellmann and Stickel state, undergo condensation, forming a closed chain of carbon and nitrogen atoms. Possibly this discrepancy is due to the different methods of reduction employed. H. G. C.

Oxidation Products of Orthodiamines and Orthoamidophenols. By O. FISCHER and E. HEPP (*Ber.*, **23**, 2787—2789; compare Abstr., this vol., p. 801).—The authors assigned the formula $NH_2 < \begin{matrix} CH \cdot C{\cdot}N \\ C_4H_4{\cdot}C{\cdot}N \end{matrix} > C_6H_4$ to the eurhodine obtained from orthophenylenediamine and benzeneazo-α-naphthylamine; corresponding compounds have been prepared from orthophenylenediamine and benzeneazoethylnaphthylamine, and benzeneazodimethylnaphthylamine, respectively. The imide formula, $NH{:}C < \begin{matrix} CH : C{\cdot}NH \\ C_6H_4{\cdot}C{=}N \end{matrix} > C_6H_4$, advanced by Kehrmann (this vol., p. 1266) for the above compound from benzeneazo-α-naphthylamine, is regarded by the authors as being a tautomeric form of their own. It is found that the action of amido-compounds on orthodiamines is not uniform; amidoazo-α-naphthylamine derivatives take part in the reaction, whilst amidoazobenzene derivatives chiefly act as dehydrogenating agents; thus diamidophenazine is obtained from orthophenylenediamine and amidoazobenzene, whilst triphenyldioxazine is formed by the action of orthoamidophenol on amidoazobenzene. J. B. T.

Fluorindine. By O. FISCHER and E. HEPP (*Ber.*, **23**, 2789—2793; compare next abstract).—The term fluorindine is applied to a class of compounds formed by heating azophenine, or almost any induline base, and also by the action of orthophenylenediamine hydrochloride on diamidophenazine, the red oxidation product of orthophenylenediamine.

FLUORINDINE FROM AZOPHENINE.—On heating azophenine alone, or with 2—3 parts of zinc-dust, *fluorindine* (*diphenylhomofluorindine*), $C_6H_4 < \begin{matrix} NPh \\ N \end{matrix} > C_6H_2 < \begin{matrix} N \\ NPh \end{matrix} > C_6H_4$ [N : N = 2 : 3 : 5 : 6], is obtained,

in cantharidine-green needles; it may be recrystallised from naphthalene, or by treatment with a mixture of alcohol and benzene for a day in an extraction apparatus. It is almost insoluble in ether, toluene, and chloroform, and imparts a characteristic fluorescence to alcohol; the solution is flame-coloured in direct light, but on adding an acid, the colour changes to greenish-blue, with a brown-red fluorescence. No definite melting point could be observed, as the compound partially sublimes on heating; the colour of the vapour is blue-violet. The compound is not acted on by hydrochloric acid at 250°, and is only partially changed by concentrated hydriodic acid at 200°. Fluorindine is a feeble base, and consequently its dyeing powers are not well developed. On boiling with alcohol and an acid, the corresponding salt is obtained; most of the salts crystallise in bronze, lustrous plates, they readily undergo dissociation, and are insoluble in water, but dissolve sparingly in alcohol with a blue colour. The *aurochloride*, $C_{30}H_{20}NH_4,HAuCl_4 + H_2O$, crystallises in iridescent, lustrous plates.

In the preparation of fluorindine by heating azophenine, a violet dye is formed as intermediate product; it is to be regarded as an *induline* with the formula $C_6H_4<{NPh \atop \underline{\quad} N}>C_6H_2(NHPh)\colon NPh$.

Fluorindine from Diamidophenazine.—Diamidophenazine (4 parts) is intimately mixed with orthophenylaminediamine (3 parts), and heated in an oil-bath, first at 173°, then for 10—15 minutes at 200—210°; the product is boiled with water, and then with dilute sulphuric acid; a greenish powder remains, from which the free base is obtained by the action of alcoholic ammonia. The compound is very sparingly soluble in all menstrua, but by prolonged boiling with a mixture of alcohol and benzene it crystallises in slender, greenish, lustrous plates; it dissolves slightly in alcohol with a red-violet colour, and the solution exhibits an intense brownish-red fluorescence. The general properties of this substance resemble those of the previous base; it has the formula $C_6H_4<{NH \atop \underline{\quad} N}>C_6H_2<{N \atop NH}>C_6H_4$, and it is proposed to term it *homofluorindine*. In all probability it is derived from the tautomeric form of diamidophenazine, $C_6H_4<{NH \atop \underline{\quad} N}>C_6H_2(NH_2)\colon NH$. These results show that the fluorindines stand in the same relation to triphenodioxazine as phenazine does to phenoxazine. J. B. T.

Action of Quinones on Orthodiamines, Orthonitraniline, and Nitroparatoluidine. By J. Leicester (*Ber.*, 23, 2793—2798; compare preceding abstract).—*Quinoneorthodinitranilide*,

$$C_6H_2O_2(NH{\cdot}C_6H_4{\cdot}NO_2)_2\ [O : NH : O : NH = 1 : 2 : 4 : 5],$$

is prepared by gently boiling quinone with orthonitraniline in glacial acetic acid solution; it crystallises from absolute alcohol in red needles melting at 305° with decomposition.

Quinonehomofluorindine, $C_6H_4<{NH \atop \underline{\quad} N}>C_6O_2<{N \atop NH}>C_6H_4$, is obtained

by heating the previous compound with alcoholic hydrogen sulphide at 100° in a sealed tube; colourless crystals are formed in the tube, which immediately become bluish-black on exposure to air; the compound is deposited from a mixture of alcohol and benzene in dark-green, granular crystals, closely resembling those of homofluorindine; the glacial acetic acid solution is blue, and exhibits an intense characteristic fluorescence, especially on the addition of a little alcohol.

Quinoneorthonitrotoluidide, $C_6H_3O_2 \cdot NH \cdot C_7H_6 \cdot NO_2$ [O : NH : O = 1 : 2 : 4], the chief product of the action of quinone on nitroparatoluidine, [Me : NO_2 : NH_2 = 1 : 3 : 4], is deposited from absolute alcohol in aggregates of red crystals, decomposing at about 300°.

Quinonediorthonitrotoluidide, $C_6H_2O_2(NH \cdot C_7H_6 \cdot NO_2)_2$, is formed together with the previous compound; it corresponds in constitution to the nitraniline derivative, is more sparingly soluble in alcohol than the previous compound, and crystallises in bronze-coloured plates which decompose at 140°.

Quinoneparamethylphenazine, $C_6H_2O_2{<}\overset{N}{\underset{N}{|}}{>}C_6H_3Me$ [O : N : N : O = 1 : 2 : 3 : 4; Me : N : N : = 4 : 5 : 6], is prepared by the action of alcoholic ammonium sulphide on nitrotoluidoquinone at 100°; it forms a bronze-coloured, crystalline powder soluble in alcohol with a violet colour; the glacial acetic acid solution is greenish-blue, and on adding dilute sulphuric acid, it acquires a faint red fluorescence.

Nitranilidotoluquinone, $C_6H_2MeO_2 \cdot NH \cdot C_6H_4 \cdot NO_2$ [O : NH : O : Me = 1 : 2 : 4 : 6], is obtained from toluquinone and orthonitraniline; it is deposited from alcohol in red crystals, which decompose at 200°. By the action of alcoholic ammonium sulphide on this compound, *quinonephenotolazine*, $C_6HMeO_2{<}\overset{N}{\underset{N}{|}}{>}C_6H_4$ [N : N : Me = 2 : 3 : 5], is produced, crystallising in small, red plates, soluble in glacial acetic acid with a green colour; the solution exhibits a red fluorescence on the addition of dilute sulphuric acid.

Nitrotoluidotoluquinone, $C_6H_2MeO_2 \cdot NH \cdot C_6H_4Me \cdot NO_2$ [NH : Me = 2 : 6], obtained from toluquinone and nitroparatoluidine

[Me : NO_2 : NH_2 = 1 : 3 : 4],

crystallises in brown plates. On reduction, this compound yields *quinonetolazine*, $C_6HMeO_2{<}\overset{N}{\underset{N}{|}}{>}C_6H_3Me$ [N : N : Me = 2 : 3 : 5], which crystallises from alcohol in small plates with a dark-red sheen; it is soluble in glacial acetic acid, the colour of the solution being green; the addition of dilute sulphuric acid causes a faint red fluorescence.

Orthonitranilidonaphthaquinone is prepared from α-naphthaquinone and orthonitraniline; it is deposited from alcohol in straw-coloured crystals, which appear carmine-red in a finely-divided state; by the reduction of this compound, the corresponding *naphthaquinonephenazine*, $C_{10}H_4O_2{<}\overset{N}{\underset{N}{|}}{>}C_6H_4$, is obtained, crystallising from alcohol in

green plates; the solution is brown, and has a faint green fluorescence. *Nitrotoluidonaphthaquinone* is formed from α-naphthaquinone and nitroparatoluidine, [Me : NO_2 : NH = 1 : 3 : 4]; it crystallises in lustrous, orange-red needles; the alcoholic solution is brownish-yellow. On reduction, *α-naphthaquinonetolazine*,

$$C_{10}H_4O_2<\overset{N}{\underset{N}{|}}>C_6H_3Me,$$

is obtained, crystallising from alcohol in steely bluish-green plates. The alcoholic and glacial acetic acid solutions are greenish-yellow, and exhibit a faint green fluorescence. The compound dissolves in concentrated sulphuric acid with a green colour. J. B. T.

Attempts to Synthesise Conhydrine. By H. ALEXANDER (*Ber.*, **23**, 2714—2715).—From the resemblance between α-pipecolylmethylalkine, $C_5NH_{10}{\cdot}CH_2{\cdot}CHMe{\cdot}OH$, and the isomeric conhydrine, Ladenburg has expressed the belief that the latter compound is likewise an alkine. In that case it would probably be an α-lupetidyl alkine, $C_5NH_{10}{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, or an α-piperidylethylalkine,

$$C_5NH_{10}{\cdot}CHEt{\cdot}OH.$$

The author has endeavoured to prepare the lutidyl compound corresponding with the first-named alkine by acting on α-picoline with ethylene chlorhydrin. A base was thus obtained the *platinochloride* of which forms well-developed yellowish-red crystals melting at 200° with decomposition, and has the expected composition $(C_8H_{11}NO)_2,H_2PtCl_6$. The free base could, however, only be prepared in aqueous solution, all attempts to prepare the anhydrous compound resulting in the formation of resinous matter. The *aurochloride* of the base, $C_8H_{11}NO,HAuCl_4$, has also been obtained, and forms small, lustrous, yellow crystals which melt at 99—100°.

An attempt was also made to prepare lupetidylalkine by acting on α-pipecoline with ethylene chlorhydrin, but without success.

H. G. C.

Strychnine. By J. TAFEL (*Ber.*, **23**, 2731—2739).—Strychnine was suspended in methyl alcohol and boiled with methyl iodide in a reflux apparatus. It was thus converted into the methiodide, which was separated and decomposed with silver sulphate. The clear solution was then treated with barium hydroxide, the excess of the latter removed by sulphuric acid, and the solution filtered, and evaporated in a vacuum. *Methylstrychnine* then separated out in colourless or faintly yellow crystals with the composition $C_{22}H_{34}N_2O_7$; these, when dried in a vacuum and finally at 108°, lost water, yielding the colourless compound $C_{22}H_{26}N_2O_3$, which is very hygroscopic and readily takes up 2 mols. of water, forming the compound $C_{22}H_{26}N_2O_3 + 2H_2O$.

Methylstrychnine, when treated with methyl alcohol and methyl iodide, readily yields a methiodide, $C_{23}H_{29}N_2O_3I$, which is insoluble in ether, sparingly soluble in hot alcohol, and more so in boiling water. It decomposes above 280° without melting, and gives a blood-red coloration with strong nitric acid. By treatment with silver sulphate

and barium hydroxide as above, it is converted into *dimethylstrychnine*, which crystallises from water in brilliant prisms with the composition $C_{23}H_{40}N_2O_9$. These lose water in a vacuum, yielding the compound $C_{23}H_{28}N_2O_3$. It dissolves easily in methyl and ethyl alcohol and hot water, very sparingly in ether; the aqueous solution is neutral, and is coloured blood-red by oxidising agents. The hydriodide dissolves in 15 parts of hot water, and crystallises from it in small plates. Its methiodide, prepared as above described, crystallises from water in colourless needles of the composition $C_{24}H_{31}N_2O_3I$, but when treated with silver sulphate and barium hydroxide, it yields, not a trimethyl-, but a dimethyl-strychnine derivative, $C_{23}H_{29}N_2O_3I$.

By heating strychnine (15 grams) with crystallised barium hydroxide (30 grams), and water (40 c.c.) for 12 hours at 140° in a tube, *strychnine dihydroxide* was formed, and precipitated by acidifying the solution with acetic acid; on dissolving the product in dilute aqueous soda and precipitating with carbonic anhydride, it is obtained in colourless needles of the composition $C_{21}H_{26}N_2O_4$.

By heating strychnine dihydrate with sodium methoxide and methyl iodide in a closed tube in the water-bath, the *methiodide* of *tetramethylstrychnine dihydroxide*, $C_{26}H_{37}N_2O_4I,2H_2O$, was obtained; it crystallises from water in long, thin needles which lose their water in a vacuum.

When working in the manner described by Loebisch and Schoop (Abstr., 1886, 814), for the preparation of "strychnol," a substance is obtained which is really *strychnine monhydroxide*, $C_{21}H_{24}N_2O_3,4H_2O$; this crystallises from water in colourless needles, and loses its water in a vacuum. C. F. B.

Crystalline Veratrine. By F. B. Ahrens (*Ber.*, **23**, 2700—2707). —In addition to the crystalline aurochloride described by Bossetti (*Arch. Pharm.*, 1883, 81), veratrine also forms a crystalline *mercurochloride*, $C_{32}H_{49}NO_9,HHgCl_3$, and *picrate*, $C_{32}H_{49}NO_9,C_6H_3N_3O_7$. The former crystallises in small, silvery plates which melt at 172° with decomposition, whilst the latter forms stable crystals which blacken at 225°, but may be heated still higher without undergoing further alteration. Both are very slightly soluble in water, but dissolve readily in alcohol.

Veratrine unites with bromine forming a *tetrabromide*, $C_{32}H_{49}NO_9Br_4$, which is an amorphous, yellow powder insoluble in water, but readily soluble in alcohol, ether, and chloroform. It readily loses 2 atoms of bromine, passing into the *dibromide*, $C_{32}H_{49}NO_9Br_2$, also a pale-yellow, amorphous powder.

The action of alcoholic potash on veratrine has been examined by Wright and Luff (Trans., 1878, 328), and that of alcoholic baryta solution by Bossetti (*loc. cit.*). The former investigators obtained tiglic acid and a new base "cevine" $C_{27}H_{43}NO_8$, whilst the latter found angelic acid and "cevidine," $C_{27}H_{45}NO_9$. The author has confirmed these results with the exception that in Wright and Luff's reaction he finds that angelic acid is first formed, and is converted by later reactions into tiglic acid. This decomposition takes place very readily, being brought about by cold aqueous potash, and also, though more slowly,

by cold dilute ammonia. It also takes place when veratrine is heated with water at 200°, a large quantity of resin being simultaneously formed.

When the alkaloïd is boiled with concentrated hydrochloric acid, it yields tiglic acid, $C_5H_8O_2$, and a lustrous, ruby-red, crystalline mass, which is probably the hydrochloride of a new base. On treatment with nitric acid, veratrine is totally oxidised; with potassium permanganate, it yields acetic and oxalic acids, and with chromic acid, acetaldehyde and carbonic anhydride. On dry distillation, it yields tiglic acid and β-picoline, the properties of which correspond with that obtained from strychnine, and differ in several points from the synthetical 2-methylpyridine. When distilled with quicklime, veratrine yields β-picoline, β-pipecoline, isobutylene, and a combustible gas not absorbed by bromine. H. G. C.

Oxidation of Ecgonine. By C. Liebermann (*Ber.*, **23**, 2518—2522).—It has been shown by Einhorn (this vol., p. 1010) that when anhydroecgonine is heated with hydrochloric acid it yields tropidine; it seemed probable, therefore, that ecgonine and tropine would give the same oxidation products under the same conditions, an assumption which is shown to be correct by the author's experiments.

When ecgonine (100 grams) is oxidised with chromic acid and sulphuric acid in the manner described by Merling (*Annalen*, **216**, 329), a brown, syrupy acid is obtained; on boiling this product with alcohol, there remains a considerable quantity (about 18 grams) of tropinic acid, identical with the compound obtained by Merling by the oxidation of tropine, and the alcoholic filtrate, on evaporation, yields a brown, semi-crystalline mass, from which an acid of the composition $C_7H_{11}NO_3$ can be isolated without difficulty.

Tropinic acid, $C_8H_{13}NO_4$, melts at 253° with decomposition (Merling gives 220—240° as the melting point), and is very readily soluble in water, but very sparingly in alcohol, and insoluble in ether and benzene; it decomposes carbonates, and seems to be a monocarboxylic acid. The *barium* salt, $(C_8H_{12}NO_4)_2Ba$, and the *calcium* salt, $(C_8H_{12}NO_4)_2Ca$, are very hygroscopic; the *zinc* salt crystallises in colourless needles, and the *lead* salt is soluble in water. The *silver* salt is very readily soluble in water, and is unstable. Tropinic acid is immediately oxidised by potassium permanganate, even in the cold. The *hydrochloride*, $C_8H_{13}NO_4,HCl + H_2O$, is crystalline, and melts below 100° with decomposition; the *aurochloride*, $C_8H_{13}NO_4,HAuCl_4$, crystallises in golden prisms, and the *platinochloride* is very readily soluble. The formation of tropinic acid from ecgonine affords fresh evidence of the close relationship existing between ecgonine and tropine.

The acid, of the composition $C_7H_{11}NO_3$, referred to above, separates from water or alcohol in well-defined crystals, melts at 117—118°, and is readily soluble in alcohol; it decomposes carbonates and forms soluble salts, but it does not reduce potassium permanganate like tropinic acid. The *silver* salt, $C_7H_{10}NO_3Ag$, is very readity soluble in water. The *calcium* salt, $(C_7H_{10}NO_3)_2Ca$, and the *barium* salt, $(C_7H_{10}NO_3)_2Ba$, crystallise in needles. The *hydrochloride* is a crystal-

line, deliquescent compound. About 14 grams of this substance are obtained by the oxidation of 100 grams of ecgonine. F. S. K.

Compounds of Hæmoglobin and Oxygen. By C. Bohr (*Compt. rend.*, **111**, 195—197).—Hæmoglobin seems to form, with oxygen, four compounds, which have the same spectrum, and similar curves of dissociation, but differ in the proportion of oxygen which they contain, namely, 0·4, 0·8, 1·7, and 2·7 c.c. of dissociable oxygen per gram. The details of the investigation will be published subsequently. C. H. B.

Physiological Chemistry.

Influence of Cooking on the Digestion of Beef and Fish. By M. Popoff (*Zeit. physiol. Chem.*, **14**, 524—532).—The foods investigated were the fresh and smoked flesh of the ox, and of the eel and sole. Quantities of these, both raw and boiled, were submitted to artificial gastric digestion; the soluble products were, after a fixed time, estimated, and the undigested residue was also weighed. The general results obtained are as follows:—

1. Raw flesh is more easily digested than that which has been boiled; this difference is more apparent with beef than fish.

2. The length of time that the boiling lasts has also an effect; indigestibility and prolonged boiling, especially in the case of beef, going together.

3. After the two varieties of flesh have been cooked equally, beef is more digestible than fish.

4. The smoking of fish favours its peptonisation; this is true for both raw and cooked smoked fish. In the case of beef, smoking has just the opposite effect.

5. Admixture of fat with fish does not hinder its digestion, as is the case with mammalian meat, but rather assists it.

The following table gives the relative digestibility, with artificial gastric juice, of the various meats used:—

	Raw.	Boiled.	Smoked.	Smoked and boiled.
Beef	100·0	83·4	71·0	60·6
Eel........	71·1	68·9	91·3	—
Sole.......	66·8	60·6	106·1	—

W. D. H.

Effect of "Saccharin" on the Digestion of Albuminoïds. By A. Stutzer (*Landw. Versuchs-Stat.*, **38**, 63—68).—Commercial saccharin is a mixture of benzoic sulphinide and about 40 per cent. of benzoic parasulphonamide. Experiments made by the author in 1884 indicated a very slight but immaterial diminution in the amount of albuminoïds digested by gastric juice. The following experiments were made with earth-nut cake, the albuminoïds of which are very

quickly digested:—(*a*) experiments with saccharin without gastric juice or hydrochloric acid; (*b*) action of varying amounts of saccharin on 100 milligrams of nitrogen, in the form of digestible albumin, in presence of 0·05 per cent. of hydrogen chloride; (*c*) same as (*b*), but with gastric juice also; (*d*) same as (*c*), but 10 per cent. and 15 per cent. hydrogen chloride were employed.

The results of experiments (*a*) show that the solubility of albuminoïds in water is considerably diminished by the presence of saccharin. The experiments with gastric juice and acid show distinctly the disturbing influence of saccharin, although the action is less marked in the experiments in which the stronger acid was used. With regard to the practical use of saccharin, the author does not draw any conclusions from the above experiments, inasmuch as the amount taken by different persons has to be considered, and individual characters play an important part in digestion. It would be of interest to determine whether both constituents of saccharin have the same action in retarding digestion, or, if not, which of them has the greater effect (compare Strohmer and Stift, *Oesterr.-Ungar. Zeitsch. f. Zuckerind. u. Landw.*, 1 Heft, 1889). N. H. J. M.

Artificial Digestion of Agricultural Feeding Stuffs. By R. NIEBLING (*Chem. Centr.*, 1890, ii, 116—117; from *Landw. Jahrb.*, **19**, 149—188).—From the results of a series of comparative experiments which the author has made between the actual digestion of a feeding stuff by the animal and the artificial digestion by means of Stutzer's method, he concludes that the latter gives too high results, the excess depending on the concentration of the acid in the pepsin. As a simpler method than that of Stutzer, the following is recommended: the substance is heated just to boiling with 0·2 per cent. of hydrochloric acid, it is then neutralised with a few c.c. of aqueous soda, and finally treated with pancreas extract. The latter redissolves the albumin, which is precipitated when the solution is neutralised.

J. W. L.

Formation of Carbamide in the Dog-fish. By W. v. SCHRÖDER (*Zeit. physiol. Chem.*, **14**, 576—598).—Städeler and Frerichs made the statement originally that the organs of the selachian fishes contain a great amount of carbamide (*J. pr. Chem.*, **73**, 48). In the present research, two varieties of *Scyllium* were investigated (*S. canicula*, and *S. catullus*), but the latter, being the larger fish, gave more satisfactory results.

The urea was estimated in the blood, muscle, and liver, with the following results:—

The blood is richer in carbamide than either the muscles or the liver; the percentage is higher even than in normal human urine. The blood, moreover, coagulates very slowly. In mammals, muscular tissue contains little or no carbamide. Five experiments were then performed, in which the liver was extirpated; the carbamide was, at periods varying from 23 to 70 hours after this operation, estimated in the muscles; the mean percentage found was then 1·86, or practically the same as in the previous experiments. The results of the experiments on normal tissues are given in the following table:

Tissue.	No. of estimations.	Percentages of carbamide.		
		Minimum.	Maximum.	Mean.
Blood	4	2·36	2·71	2·61
Muscle	5	1·82	2·16	1·95
Liver	7	1·01	1·89	1·36

How to explain the occurrence of so great an amount of carbamide in the body of these animals is a difficult matter: the most probable reason, however, appears to be sluggishness of the kidneys in excreting the carbamide which is formed. W. D. H.

Colouring Matter of Purpura lapillus. By A. LETELLIER (*Compt. rend.*, **111**, 307—309).—The appearance of the colouring matter (Abstr., 1889, 1207) is accompanied by the development of a penetrating odour closely resembling that of allyl sulphide. *Murex brandaris* and *M. trunculus* develop a very similar odour. The smell is also perceived when the crystallised photogenic compounds (*loc. cit.*) are exposed to light, and it is, therefore, not due to putrefaction of the fascia. No allyl sulphide could be definitely isolated from 6,000 fasciæ, but ether extracted a substance which contained sulphur, evolved ammonia when heated with alcoholic potash, and gave the cyanide reaction with ammonium sulphide and a ferric salt. Allyl sulphide is usually accompanied by the thiocyanate in the juices of plants, and probably this is also the case in the fasciæ of *Purpura lapillus*. Some evidence was also obtained of the presence of carbamides or thiocarbamides in the water which had contained the fasciæ, but this fact was not definitely established. C. H. B.

Animal Melanins and Hæmosiderin. By J. J. ABEL (*Chem. Centr.*, 1890, i, 1007—1008; from *Arch. path. Anat.*, **120**, 204—217). Besides egg-albumin and bilirubin, which are formed from the hæmoglobin as the blood issues from the surrounding cartilage, dark-brown or black and colourless substances are formed, in which iron may be detected by means of ammonium sulphide and potassium ferrocyanide. The author concludes from this that the blue coloration observed on mixing blood with hydrochloric acid and potassium ferrocyanide is due to the presence of iron albuminate.

The composition of the black substances, the so-called pigments, is still unknown. The alkaline solutions of the animal carbohydrates give, with solutions of ferric salts, precipitates, from which the iron cannot be again separated, and the author, therefore, concludes that, because iron may be found present with the black pigments, it does not follow that it is contained in them. J. W. L.

Physiological Action of Thallium Salts. By J. BLAKE (*Compt. rend.*, **111**, 57—59).—Thallous salts injected into the veins act only

on one nervous centre, namely, that controlling the pulmonary ganglions, whilst the thallic salts, under the same conditions, affect all the nervous centres. The author considers that this difference in behaviour, and the poisonous action of metallic salts generally, is connected with the vibratory movements of the metals as shown by the spectroscope. In thallous salts the metal is univalent, and its atoms have only one set of harmonic vibrations, whereas in thallic salts the metal is trivalent, and its atoms or molecules are the *locus* of several sets of harmonic vibrations. C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Reducing Power of Micro-organisms. By L. de Blasi and G. R. Travali (*Gazzetta*, **20**, 18—24).—The authors, in reply to some strictures of Leone's (*Gazzetta*, **19**, 504) on a former paper of theirs (*Gazzetta*, **19**, 440), maintain that ammonia is the only ultimate product of the decomposition of albumin by the micro-organisms which they examined. They consider the action of the germs to be throughout reducing, nitrification being a purely chemical phenomenon.

To ascertain whether any oxidising germs exist in the atmosphere, the authors have repeated Leone's experiments (Abstr., 1887, 615): two flasks each containing a litre of spring water and 6 drops of nutritive gelatin, and two similar flasks containing only 1 drop of gelatin, were exposed to the air for 80 days. Nitrous acid was detected in the liquids on the second day, and increased in quantity up to the 18th day, when it commenced to diminish, and finally disappeared on the 22nd, or in one or two cases on the 31st day. Traces of nitric acid were present in the water when taken; the amount gradually increased and diminished concurrently with the nitrous acid, only the original traces eventually remaining. Ammonia was found on the second or third day, increasing in quantity with the diminution of the nitric and nitrous acids; the amount ceased to vary after the 60th day.

Determinations of the nitrogen in the gelatin taken, and in the ammonia finally obtained, gave almost exactly the same results, showing that the conversion of the nitrogen into ammonia is quantitative. S. B. A. A.

Reduction of Nitrates by Micro-organisms. By T. Leone (*Gazzetta*, **20**, 98—104).—The author has previously shown (Abstr., 1887, 615) that the power of reducing nitrates is common to a great number of germs when placed in conditions favourable to their development; in a solution of nutritive gelatin, for instance, the nitrates are at first destroyed either directly or with the intermediate production of nitrites; when, however, the nutriment is exhausted,

nitrification of the ammoniacal compounds in the solution commences.

The quantitative determinations now made by the author prove that the nitric acid in nitrates is reduced to nitrogen gas, and is not converted into ammonia as generally supposed; a definite amount of ammonia is always produced by the growth of the germs, but this is the same whether the menstruum contains nitrates or not, the only difference being that, in the former case, the total formation of ammonia is more speedily effected. The nitrogen in nitrates is not absorbed by the germs, but is quantitatively evolved from the solutions in the free state.

The author has also observed that putrefaction is accelerated by the addition of a small quantity of a nitrate, but when more is added than is sufficient for the decomposition of the organic matter present, the excess is not acted on. It would, therefore, seem that nitrates are utilised by micro-organisms as sources from which they can draw a supply of oxygen for the decomposition of their organic nutriment more conveniently than from the atmosphere.

S. B. A. A.

Action of the Bacillus of Malignant Œdema on Carbohydrates. By R. Kerry and S. Fränkel (*Monatsh.*, 11, 268—271; compare this vol., p. 542).—The bacillus was cultivated in flasks containing grape sugar (150 grams), peptone (7·5 grams), Kemmerich's meat extract (15 grams), and feebly ignited calcium carbonate (75 grams) in 3 litres of water; the air in the flasks was displaced by carbonic anhydride.

The products obtained by adding oxalic acid and distilling were alcohol and butyric acid, whilst fermentation lactic acid and a little sarcolactic acid (from the meat extract) were left in the residue in the retort.

Nencki and Sieber (this vol., p. 78) obtained only butyl alcohol during the fermentation of sugar, while the authors obtain only ethyl alcohol, a difference to be accounted for by the individual nature of the bacillus employed.

A. G. B.

The Formation of Hydrogen Sulphide during the Alcoholic Fermentation. By L. Sostegni and A. Sannino (*Chem. Centr.*, 1890, ii, 112; from *Staz. sperim. agric. ital.*, **4**, 434—447).—The authors fermented a sugar solution with a pure yeast culture. Flowers of sulphur were added, and hydrogen sulphide (which has frequently been observed during the fermentation of such solutions) was formed. The presence of air retarded the formation of hydrogen sulphide, but assisted the formation of alcohol. Since the yeast used was from a pure culture, the possibility of other ferments, causing the formation of sulphur, is excluded.

J. W. L.

Production of Ethereal Salts by Fermentation. By G. Jacquemin (*Compt. rend.*, **111**, 56—57).—Two equal quantities of sterilised barley wort were inoculated with a liquid which contained the lactic ferment, *Saccharomyces*, and the butyric vibrion, and one part

was allowed to ferment with free access of air, whilst the other was kept out of contact with air, although the gases produced could escape.

In the first case, the lactic fermentation took place; in the second, the liquid contained only traces of lactic acid, but yielded a somewhat high proportion of ethyl butyrate and of ethyl alcohol and its higher homologues. When the air is excluded the butyric vibrion, which is anaërobic, flourishes, but the lactic ferment, which is aërobic, loses its activity. The butyric acid produced by the vibrion, and the alcohol produced by the *Saccharomyces*, react at the moment of their formation, and yield ethyl butyrate.

In a similar manner, if pure *Saccharomyces ellipsoïdeus* is added to barley wort undergoing active lactic fermentation, ethyl lactate is formed.

C. H. B.

Fat-decomposing Ferments in Plants. By W. SIGMUND (*Monatsh.*, **11**, 272—276).—It was found that when oily seeds were macerated and shaken with water, the emulsion which was obtained contained more free fatty acid after some hours than it did at first, and from this it was concluded that some fat-decomposing ferment must have been present.

To isolate the ferment, the seeds (rape and castor-oil) were macerated with glycerol or water, and the extract precipitated with alcohol; the precipitate was washed with alcohol, dried at 30°, and finely powdered; a weighed quantity (0·2—0·5 gram) of it was then shaken with water and a weighed quantity (5—10 grams) of an oil (rape-, olive-, and castor-oils), and the emulsion allowed to stand for 24 hours, after which time the free fatty acids were titrated with decinormal soda and turmeric. The acidity of the oil was determined before the experiment, and a blank determination made at the same time as the other. In this way it was found that free acid was always produced by the alcohol precipitate; the results are tabulated in the paper, and, as an example, it may be quoted that 0·20 gram of alcohol precipitate from summer rape seed, acting on 5 grams of colza oil, produced acid equivalent to 51 milligrams of oleic acid.

As the alcohol precipitate might be pure albumin, and as albumin is known to more or less accelerate the decomposition of fats, experiments were performed, exactly as above, with pure egg albumin, but the amount of free acid found, after 24 hours, was very small.

A. G. B.

Fermentation and Composition of Cranberry Juice. By E. MACH and K. PORTELE (*Landw. Versuchs-Stat.*, **38**, 69—78).—Cranberry juice was allowed to ferment with yeast for nine days, either without further addition or with addition of grape must, and the alcohol determined. The results show that the juice will not ferment, and that this is caused by a substance present in the juice, and not in the skin, &c., of the berries. Similar results were obtained when a mixture of cranberry juice and must (equal vols.) was left to ferment; after 14 days, there was no sign of fermentation. With cranberry juice (1 part) and must (2 parts), fermentation began in 9 days, and in 14 days 3·88 per cent. of alcohol was formed. Löw

(*J. pr. Chem.* [2], **19**, 312) showed that cranberries contain benzoic acid, and pointed out that this might be the reason that they do not decay for so long, and the author's experiments confirm this view. Neither oxalic, succinic, tartaric, nor salicylic acid is present.

The sp. gr. of cranberry juice from Bozen and from Hall varied between 1·0521 and 1·0661.

The following numbers show the amounts of different constituents in grams per litre of juice of cranberries, examined in 1888, from (A) Bozen, and (B) Hall:—

	Invert-sugar.	Total acid as malic acid.	Benzoic acid.	Tannic acid.	Nitrogen.	Ash.
A. Fresh berries—						
(*a*), 26th Sept. ..	92·00	19·11	—	2·24	0·12	2·98
(*b*), 6th Oct.	79·20	18·04	0·862	—	0·11	—
Soft berries—						
(*c*), 13th Nov. ...	118·00	19·92	—	—	—	—
B. (*d*), healthy, fresh, and hard, 14th Nov.	90·20	18·84	0·638	—	0·101	—
(*e*), soft and dried up, 14th Nov.........	116·70	20·55	—	—	—	—

Juice from (*d*), examined later (21st March, 1889), contained: invert-sugar 73·80, total acid 22·33, volatile acid (as acetic acid) 3·25, alcohol 1·04, and ash 3·64 grams per litre. Juice from (*e*) contained, on 10th December, 1889, invert-sugar 41·10, acid 34·18, benzoic acid 0·759, volatile acid 15·20, and alcohol 3·42 grams per litre. The ash of (*a*) contained phosphoric acid 3·11, and potash 47·64 per cent.

Malic and citric acid may be present in considerable quantities.

Classen found that the bitter substance present in cranberries was identical with arbutin (*Jahresber. Agr. Chem.*, 1885, 362); in a subsequent examination of American cranberries, he could not detect arbutin, but found a substance (oxycoccin) which gave similar reactions to arbutin (*Bied. Centr.*, **16**, 70).

The fruit and leaves of *Arctostaphylos uva ursi* do not contain benzoic acid. The arbutin which is present has no preservative action. Cranberry leaves contain no benzoic acid. N. H. J. M.

Chemical Composition of Vegetable Cell-membrane. By E. Schulze (*Ber.*, **23**, 2579—2583).—The investigations of Steiger, Maxwell, Reiss, and the author have shown that many cell-walls contain not only a substance which is insoluble in dilute acids, and which, from its behaviour, is considered to be cellulose, but also certain carbohydrates which are quickly dissolved and decomposed by hot dilute acids, yielding galactose, mannose, and pentaglucoses.

The author has examined the insoluble cellulose of various vege-

table products in order to determine whether it gives any other sugar than glucose on hydrolysis. The cellulose examined was obtained from skinned peas and lupine seeds, from coffee berries, wheat-bran, cocoa-nut, and the skins of lupine seeds; after removing the fat, albuminoïds, &c., the residual cellulose was treated with strong sulphuric acid, as described by Flechig. The syrupy sugar prepared in this way, on oxidation with dilute nitric acid, gave saccharic acid in all cases, proving the presence of glucose; this result is in accordance with the view that cellulose is a polymerised anhydride of glucose. Further experiments proved that in some cases, at least, cellulose does not consist entirely of such an anhydride of glucose; the pure cellulose obtained from the seed-skins of lupines is coloured an intense violet-red when it is boiled with phloroglucinol and hydrochloric acid, and when the coloured substance is placed in a 50 per cent. solution of chloral, the latter also became coloured violet-red; cellulose from cotton-wool does not show this behaviour.

The cellulose from the seed-skins of lupines gives considerable quantities of furfuraldehyde on distillation with sulphuric acid, a fact which indicates the presence of a pentaglucose, but on hydrolysis with strong sulphuric acid, glucose is the only sugar that is produced.

The cellulose from coffee berries does not consist entirely of a polymerised anhydride of glucose, as, on hydrolysis with strong sulphuric acid, it yields a considerable quantity of mannose as well as glucose. Cocoa-nut cellulose seems to give the same two sugars under the same conditions, but the quantity of mannose produced is very small. F. S. K.

Cholesterin in Plants. By E. Schulze (*Zeit. physiol. Chem.*, **14**, 491—521).—The author, with J. Barbieri (Abstr., 1882, 1202), previously stated that lupine seeds and etiolated lupine seedlings contain cholesterin; the cholesterin was isolated, and weighed in a crystalline condition; further, it was shown that the percentage and total amount of cholesterin was greater in the seedlings than in the seeds, and the conclusion was therefore drawn that cholesterin is not one of the substances used up in the dark during the process of germination. Burchard (*Dissert.*, *Rostock*, 1889) has, however, challenged this assertion; for, experimenting with grass seeds, he found that the proportion of cholesterin in the seeds was greater than in the seedlings. He considers that in the experiments of Schulze and Barbieri the cholesterin was contaminated with impurities. The method by which he estimated cholesterin was the intensity of the colour reaction, described by Liebermann as the cholestol reaction; this is a green, fluorescent colour produced by the addition of acetic anhydride and concentrated sulphuric acid to a solution of cholesterin.

The present paper is largely polemical; it points out that Burchard experimented with grass and linseed, and not with lupines; that any evidence of the presence of impurities in the cholesterin obtained by Schulze and Barbieri is not only wanting, but that the evidence is all the other way; that the colorimetric method adopted by Burchard is

rough and misleading, especially when used, as Burchard did use it, with impure extracts, that is, extracts containing fats and other substances which give tints with the reagents employed; that new experiments, details of which are given, confirm the older statements originally made; and lastly, that this is true not only for lupines, but also for the grasses and other plants used by Burchard.

W. D. H.

Poison of Corn Cockle Seeds (Agrostemma githago, Githago segetum). By LEHMANN and MORI (*Ann. Agronom.*, **16**, 381—382). —Corn cockle seed has been long recognised as poisonous. It contains, albuminoïds, 14·46; fat, 7·09; starch, 47·87; saponin, 6·56; cellulose, 8·23; ash, 3·97; water, 11·50 = 99·68. The saponin is the poisonous ingredient; apart from this, the seed is very nutritious. Fowls, pigeons, ducks, &c., die after eating these seeds; large doses are dangerous to cats, dogs, and pigs. Calves die after 18—20 hours when given 6—7 grams per kilo. of live weight; they recover after 4 grams per kilo. 3 to 5 grams of the flour produced symptoms of poisoning in the authors. The poisonous property is destroyed by baking or grilling the seed or flour in a stove; an aromatic odour is given off, and in the heated substance no saponin can be detected. One of the authors consumed 100 grams, the other 140 grams, of the cooked flour in 17 days, once as much as 35 grams in two days, without feeling the least ill effect.

J. M. H. M.

Combustibility of Tobacco. By A. MAYER (*Landw. Versuchs-Stat.*, **38**, 127—139).—In order to observe the effect of different substances, organic and inorganic, on the combustibility of paper, ordinary filter paper was soaked in 0·5 per cent. solutions. Paper soaked in tannin, peptone, resin, oxalic acid, sugar, glycerol, starch, dextrin, olive oil, calcium nitrate, and potassium hydrogen phosphate, burnt with flame, and offered resistance in putting out the flame. When paper was treated with potassium and sodium chloride, carbonate, and sulphate, potassium nitrate and citrate, sodium acetate and phosphate, and burnt, the flame was readily extinguished. On the other hand, the papers which burn well with a flame generally cease to glow within 10 seconds after the flame was put out, and those which burn badly (with a flame) will glow for over 100 seconds.

Organic substances of the most different kinds are favourable to combustion with flame and diminish the power of glowing, whilst inorganic substances generally have the opposite effect. The salts which are most favourable for glowing are: alkaline nitrates, sulphates, and carbonates, alkaline organic salts, and potassium chloride. Sodium salts have less effect than potassium salts, and calcium and magnesium salts much less still.

Dark ashes, containing carbon, were produced with paper treated with sodium nitrate, sulphate, phosphate, and borate, and with potassium phosphate and calcium chloride. Paper treated with potassium salts, magnesium sulphate, and sodium carbonate gave white ashes. With regard to the favourable effect sometimes produced by chlorides, it is suggested that this may be caused by a

reduction of the salt, and the decomposition of water by the chlorine with liberation of oxygen. The fact that chlorides are favourable rather than unfavourable for the glowing of paper is of importance, and it may be assumed that this also holds good with tobacco. The more ash constituents tobacco contains, and the more potash present in the ash, and the less potash combined with fixed acids, the better the tobacco will burn. On the other hand, tobacco will burn badly when much phosphoric acid and lime are present; and the presence of much calcium chloride and sulphate is also unfavourable. The following table shows the percentage of some constituents in tobacco, of different qualities, from Sumatra:—

	Chlorine.	Potash.	Free alkali as K_2CO_3.	Ash.	Nitrogen.
Good	1·5	5·9	4·9	20·5	2·7
Sufficiently good (light ash)	0·5	5·8	6·8	20·8	3·2
Sufficiently good	0·7	6·6	5·5	22·5	2·0
„ „ (grey ash)	1·2	7·9	4·1	17·7	3·3
Bad	3·3	4·6	0·5	18·5	2·6

The amount of free alkali is a better measure of combustibility than the amount of chlorine.

Tobacco which burns badly can be readily made to burn well by keeping for 24 hours in 0·5 per cent. potassium acetate or nitrate, and then drying. In this way soluble organic matter and the soluble chlorides are extracted, whilst the salts favourable to glowing are taken up. By using 0·5 per cent. solution of calcium acetate, the most incombustible tobacco, which can otherwise only be used for snuff, can be made to burn well and yield a quite white ash.

N. H. J. M.

Exhaustion of Cultivated but Unmanured Soils: Drainage Waters. By P. P. Dehérain (*Compt. rend.*, **111**, 253—259).—Comparison of the volume of the drainage water with the volume of the rain, and analysis of the former, show that the sterility of unmanured soil (this vol., p. 406) cannot be attributed to any alteration in its power of retaining moisture, or in its capacity to furnish nitrates.

In order to avoid the great loss of nitrates in the drainage water which takes place in the late summer and autumn, the author suggests planting colza, rape, or some other rapidly growing crop, which, at the end of autumn or in the spring, is worked into the soil, and not only returns to it the nitrogen which would otherwise have been lost, but also furnishes a very beneficial organic manure.

C. H. B.

Composition of Straw. By A. Hébert (*Ann. Agronom.*, **16**, 358—371).—The author quotes the following analysis, made after methods long in use, to show the indeterminate state of our know-

ledge of the actual composition of straw:—Water, 14·05; ash, 6·98; nitrogenous substances, 3·12; crude fatty matters (ether extract), 0·99; sugars, 0·27; pectic substances, 0·70; crude cellulose, 31·40; starch and similar substances, 17·36; undetermined substances, 25·13—100·00. The weakness lies in the last two items. "Starch, &c.," is usually calculated from the quantity of reducing sugar produced by heating with an acid. The sugar produced in this way is a very indefinite quantity, varying with the treatment adopted; it may be, and is, produced from many substances other than starch; and, moreover, starch cannot be detected by the microscrope in the tissues of straw. Guided by Wheeler and Tollens' recent discovery of wood-gum, a substance which yields a special sugar, xylose, on hydrolysis with acids, the author has applied their process to straw, and has succeeded in extracting the same or a similar substance, namely, straw-gum, also yielding xylose on hydrolysis. The gum is obtained by extracting the straw for 48 hours with 5 per cent. soda in the cold, precipitating with alcohol, treating the precipitate with hydrochloric acid, repeatedly washing with alcohol, and drying.

The xylose produced from this gum by the action of dilute acids has the formula $C_5H_{10}O_5$, melts at 153—154° (the xylose of Wheeler and Tollens melts at 144—145°), is very soluble in water, soluble also in alcohol, reduces Fehling's solution, crystallises in prismatic needles, has a rotatory power of +18·63°, and a molecular weight of 146, determined by Raoult's cryoscopic method. On treating this sugar with phenylhydrazine hydrochloride and sodium acetate, crystalline needles are formed melting at 152—155°, very soluble in alcohol, less soluble in acetone, slightly soluble in water, characters identical with those of the xylosazone of Wheeler and Tollens formed in a similar manner. In accordance with this discovery of straw-gum, the author finds that, on distillation with diluted sulphuric acid, straw yields furfuraldehyde identified by conversion into furfuramide. Wheat straw and oat straw both yield these products.

As regards the "undetermined substances," Muntz has concluded that amongst them must be a substance richer in carbon than the carbohydrates; this substance is, according to Deherain, the vasculose studied by Frémy. If from the total carbon, hydrogen, oxygen, and nitrogen found in straw are deducted the quantities of these elements contained in the known constituents, the residue has the percentage composition C 50·13, H 6·19, O 43·68. The constituent yielded by straw to the action of alkalis, and precipitable by hydrochloric acid, has for every 50·13 C, 4·86 of hydrogen, and 31·88 of oxygen = 86·87. Supposing the difference between 100 and 86·87, namely, 13·13, to consist of water (1·46 H + 11·67 O), and adding this to the previous figures, we get C 50·13, H 6·32, O 43·55 = 100·00, agreeing almost exactly with those of the undetermined straw residue, which, therefore, is concluded to consist of hydrated vasculose. The author has devised the following method of analysis to take account of the vasculose and straw-gum. After determining by old methods the moisture, ash, nitrogenous substances, and substances soluble in water and in ether, 2 grams of the straw exhausted by ether and by water are placed in a tube, 70 to 80 c.c. of 10 per cent. sodium hydrate

solution is added, the tube sealed before the blowpipe, and heated in a paraffin- or oil-bath at 120° for three hours. During this treatment, the cellulose remains intact, the gum and vasculose dissolve. After cooling, the tube is opened, and its contents diluted to 150—200 c.c., filtered, the cellulose washed until free from alkali, dried at 110°, weighed, calcined, and the ash deducted. The filtrate is neutralised exactly by hydrochloric acid (turning from brown to light-yellow at the moment of neutralisation), evaporated to dryness on a water-bath, together with any precipitate which forms, and the residue treated with distilled water. The vasculose, which has been rendered insoluble by the drying, is left as a dense, granular residue, which is filtered, washed, dried at 110°, weighed, calcined, and the ash deducted. The straw-gum remains in the filtrate, to which, after concentration, 5 per cent. of hydrochloric acid is added, and the liquid heated in a closed vessel at 108° for two hours, or on a water-bath for five hours. The sugar in the filtered liquid is estimated by Fehling's solution, 10 c.c. of which = 45·4 milligrams of xylose = 48 milligrams of invert sugar. As the composition of the pure gum is unknown, it is reckoned as xylose in the analysis, and as xylose is a product of hydrolysis, the total obtained in this way is often a little over 100. The following analyses were made by this method:—

	Wheat straw.	Oat straw.
Water	10·40	8·05
Nitrogenous substances	2·42 (N = 0·388 p. c.)	3·57 (N = 0·571 p. c.)
Ether extract	1·18	2·98
Water extract, less ash (sugars, gum, tannin)	3·37	5·70
Cellulose	33·60	27·15
Vasculose	24·00	14·20
Straw-gum, reckoned as xylose	19·71	27·70
Ash	6·34	9·85
	101·02	99·20

J. M. H. M.

Analytical Chemistry.

New Method of Colour Analysis by Means of the Tintometer. By J. W. Lovibond (*J. Soc. Chem. Ind.*, 9, 10—15). The instrument and method referred to in the paper is a new means of impartially judging the various colours, for recording the factors of colour which combine to form any given colour; and a system for registering the same, even in the most complicated combinations, and the most delicate shades, as well as in the deepest tints, which exist in nature. The instrument consists of two tubes, side by side,

divided by a central partition terminating at the centre of the eyepiece in a knife edge, which, being inside the range of vision, is not noticed, so that light entering the openings at the opposite end, passes in equal quantities up each tube to the eye of the observer, giving a clear view of any opaque substances which may be placed outside or of transparent substances inside the tubes. The sides and central partition are grooved, in order to hide the edges of the measuring glasses, and of the gauged vessels for containing the liquids. Stops are placed at convenient distances to cut off light reflected from the sides, and the size and shape of the apertures introducing the light can be altered by means of diaphragms to suit small or irregularly shaped samples. The standard scale in connection with the apparatus consists of sets of coloured glass slips, all the glasses of each set being of the same colour, but each glass differing in depth of colour, the difference being in degrees of equal value throughout the scale. In all comparisons of a single colour, the starting point has been taken as a pure white. The standard used as a background for the glasses is pure calcium sulphate for small surfaces, and for large surfaces, as for the reflectors, the smooth side of Chance's opal glass. The new method is founded on the fact that neutral grey under certain conditions is always made by a combination of 1 red, 1·2 yellow, and 2·4 blue in the original scales, and these proportions hold good at all depths. Then, by assuming these combining values of red, yellow, and blue to be units of their respective colours, a simple relationship of equality between these three primary colours is established, at least so far as the production of neutral grey is concerned. Having established this common equivalent as a unit of colour in reference to neutral grey, by removing the yellow equivalent a normal purple is left, by removing the blue a normal orange, and by removing the red a normal green, each being made up of equivalents of the two remaining primaries. If binary colour is taken to be the sum of any two colours composing it, then any departure from the normal towards either primary can be accurately measured and described. When a colour is composed of the three primaries, the units of neutral grey may be deducted as such, and the balance looked on as free colour. It also follows that by constant addition of neutral grey tints, a scale of equal degrees ranging from white to black may be established, and made available for measuring the penetrating power of light. The proportion of primary colours for the neutral grey standard the author has been dealing with is the result of observations taken in the open air, under a dull grey sky with light as nearly perpendicular as possible reflected from Chance's opal glass, and is the average of 324 observations made by nine persons. It was also found that all kinds of ordinary daylight between the first approach of twilight and direct rays from the sun are available for ordinary work, so that variations in the colour of daylight within wide limits do not alter the readings where the same light is used for both sides. D. B.

Oxidation of the Sulphur in Carbon Compounds. By BERTHELOT, ANDRÉ, and MATIGNON (*Compt. rend.*, **111**, 6—9).—The sub-

stance is burnt, in presence of water (10 to 15 c.c.). in a calorimetric bomb containing oxygen under a pressure of 25 atmos. All the sulphur is converted into sulphuric acid, and it is only in the case of compounds containing very little hydrogen that any sulphurous acid is found in the bomb. In order to ensure complete combustion, substances of this character are mixed with a known weight of pure camphor.

The following determinations of sulphur were obtained by this method: egg albumin, 1·65, 1·59, and 1·59 per cent.; gluten, 0·90; wheat fibrin, 0·97; vitellin, 1·26; fibrin from calf's blood, 1·17; purified wool, 3·71 and 3·59. As examples of the applicability of the process to compounds rich in sulphur, the following results are given: thiophen, 38·06 and 38·07 (calc., 38·09); taurine, 25·4 and 25·3 (calc., 25·6); carbon bisulphide, 84·05 (calc., 84·2).

C. H. B.

Wiborgh's Method for the Estimation of Sulphur in Iron and Steel. By J. B. COHEN (*J. Soc. Chem. Ind.*, **9**, 16).—The apparatus consists of a wide-necked flask, holding from 250 to 300 c.c., to which is fitted a double-bored cork. Through one hole, a tap funnel is passed which terminates just below the cork, and through the other a cylindrical glass tube about 21 cm. long, open at both ends; the upper end of the latter is about 6 cm. in diameter, and the lower end is drawn out so as to pass through the hole in the cork. The amount of sulphur is determined by the depth of the yellow stain produced by hydrogen sulphide on the surface of a piece of calico previously soaked in a 5 per cent. solution of cadmium acetate and dried, the calico being stretched across the wide open end of the glass tube. The flask is first half-filled with water, and boiled on a sand-bath to expel air, the iron or steel (0·1 to 0·8 gram, according to the amount of sulphur) is quickly introduced, and the water again boiled for a few minutes, dilute sulphuric acid (1 in 5) is added gradually from the tap funnel, without interrupting the heating, until the iron is dissolved. Hydrogen sulphide is evolved, and this stains the calico. When the iron is completely dissolved, the boiling is continued for about 10 minutes, after which the calico is removed, well rinsed, and dried. The stain is then compared with a set of standards mounted on white cardboard, and kept for comparison. The weight of sulphur is determined by the following formula:—If w is the weight of the standard corresponding with the standard shade containing s of sulphur, and w_1 the weight of the sample taken, then the weight of sulphur s_1 in the sample is $s_1 = \frac{ws}{w_1}$.

D. B.

Determination of Sulphur in Iron and Steel. By L. ARCHBUTT (*J. Soc. Chem. Ind.*, **9**, 25—27).—5 grams of steel or iron is added to a previously heated mixture of 40 c.c. hydrochloric acid (1·10) and 20 c.c. nitric acid (1·42) contained in a large, lipped beaker; when the effervescence has ceased, a few crystals of potassium chlorate are added, and the solution is evaporated to complete dryness, and heated on the hot plate for at least half an hour, turning the beaker round occasionally so as to dry every part equally. When cold,

the residue is heated with 20 c.c. more hydrochloric acid and again thoroughly dried; 40 c.c. of hydrochloric acid are then added and heated until a clear solution is obtained. The liquid is now cautiously evaporated until a skin begins to form, when the beaker is removed from the plate, 5 c.c. of hydrochloric acid is added, and boiling hot water is blown in from a wash-bottle until the solution is about double in volume. It is then at once poured on to a 10-cm. filter, which it just about fills, the beaker is rinsed two or three times with a very little more hot water, and the filter is covered up and allowed to drain. It is now washed, say twice, with cold water, and removed to another glass, where the rest of the silica remaining in the beaker is rinsed on to it and washed for the silicon estimation. The dark-coloured filtrate containing the sulphur as sulphuric acid, which should be less than 70 c.c. in bulk, is treated with 5 c.c. of a 10 per cent. solution of barium chloride, and left over night in the cold, or it is heated and filtered as soon as the precipitate has completely subsided. The solution is filtered, with or without suction, through a paper which has been previously washed with hydrochloric acid (which greatly hastens filtration) and the precipitate washed with cold water, dried, ignited, and weighed. From the weight is deducted that of the barium sulphate obtained in a blank experiment with the same quantities of hydrochloric and nitric acids. The precipitate is seldom, if ever, contaminated with iron, although the ash of the paper is generally pink. If there is any excess of iron present, it is easily estimated by heating the precipitate with hydrochloric acid, diluting, and making a colour titration with potassium thiocyanate. Some experiments were made for the purpose of comparing the results obtained by this method with those yielded by the evolution process, and it was found that whether the iron or steel is oxidised directly with aqua regia, or whether the sulphur is evolved as hydrogen sulphide, practically the same results are obtained; this supports the conclusion that a concentrated solution of ferric chloride, whether nearly neutral or strongly acid, has no appreciable solvent action on barium sulphate in the presence of barium chloride.

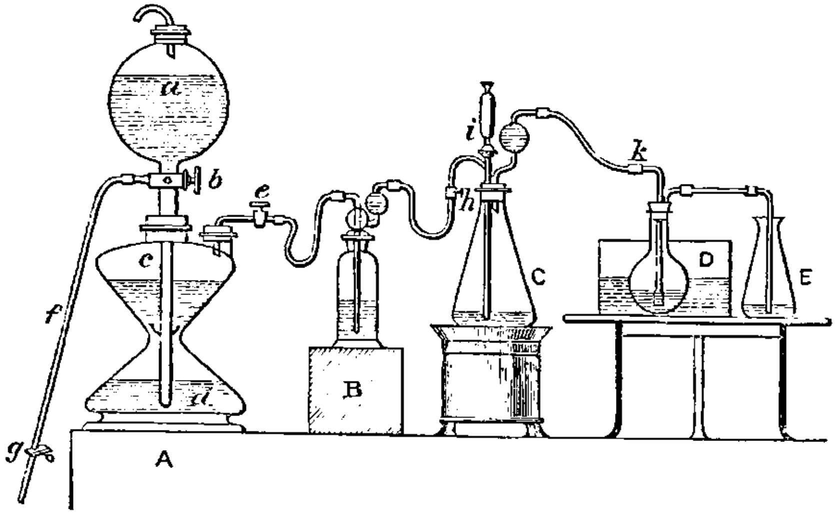
D. B.

Rapid Gravimetric Determination of Sulphur in Iron and Steel. By C. Reinhardt (*Chem. Centr.*, 1890, ii, 79—80).—The author recommends the use of the following method as being much more rapid for the determination of sulphur in iron and steel than those usually employed.

The apparatus cousists of the following parts: a modified Kipp's hydrogen generator, A, a Drechsel's washing flask, B, an Erlenmeyer flask, C, an absorption flask, D, and a flask, E, used to test the gas as it issues for any traces of hydrogen sulphide which may have escaped absorption in D. The Kipp's generator has a three-way cock, *b*, to which is attached the tube *f*, by means of which the acid may be siphoned off when too far neutralised to be of further use. The Erlenmeyer flask has an acid-funnel, *i*.

The reagents required are: (1) soda containing a certain amount of sulphate, 500 grams of pure sodium hydroxide purified by alcohol,

is dissolved in 2,000 c.c. of water, and after standing for several days, the clear solution is siphoned off into a well closed flask, carrying through its stopper a 100-c.c. pipette which reaches nearly to the bottom. Sulphuric acid (1 : 4) is added until 100 c.c. of the mixture



contains sulphate equal to about 0·1000 gram of barium sulphate; (2) alkaline arsenious acid solution 10 grams is dissolved in 25 c.c. of ammonia (10 per cent.), and 175 c.c. of water by the aid of a gentle heat; (3) potassium permanganate, 6 grams in 1000 c.c. of water, used in B to purify the hydrogen. Before making a determination of the sulphur in iron, the exact amount of the sulphuric acid which 100 c.c. of the soda solution contains is determined in the same manner as the actual determination of the sulphur in the iron is carried out.

Of pig iron, 5 grams with 60 c.c. of hydrochloric acid, of cast iron or wrought iron, 10 grams with 100 c.c. of hydrochloric acid, is employed. The iron is placed in the flask C with 10 c.c. of water. The acid is put into the funnel above. 100 c.c. of the soda solution is put into the absorption flask D. Acid is now run in carefully from the funnel, and a slow current of hydrogen is passed through the apparatus from the generator A. After all the acid has been run into C, the liquid is brought to boiling. The hydrogen sulphide evolved from the iron is thus carried over into D, being there absorbed by the soda. At the conclusion of the reaction, this is transferred to a 500 c c. flask, the sulphide oxidised with 20 c.c. of bromine-water, and after rendering acid with hydrochloric acid (sp. gr. = 1·19), it is heated to boiling, precipitated with 10 c.c. of barium chloride solution, the excess of bromine reduced with arsenious acid, allowed to remain for two hours, and the barium sulphate and the precipitate collected, washed, dried, and weighed.

The author recommends the employment of soda containing sulphate, because of the difficulty frequently experienced in filtering small quantities of barium sulphate perfectly. J. W. L.

Comparison of the Methods in Use for Estimating Organic Nitrogen. By R. W. ODDY and J. B. COHEN (*J. Soc. Chem. Ind.*, **9**, 17).—The methods compared were those of Kjeldahl, Wanklyn, and Dumas. Colourless isinglass was selected as a typical albuminoïd substance. The analysis by Dumas' method gave the following percentages of nitrogen :—15·28, 15·29, 15·93, 15·22, and 15·74. As this method always gives too high a result, due to the difficulty of completely expelling all air from the tube, 15·2 per cent. may be taken as a close approximation to the truth. A portion of the same sample of isinglass was dissolved in water, and the amount of albuminoïd ammonia determined exactly as described by Wanklyn in his book on water analysis. The authors found 12·75 per cent. of ammonia; Wanklyn gives 12·7 per cent. equivalent to 10·5 per cent. of nitrogen. As might have been anticipated, the percentage is much too low. Kjeldahl's process gave the following results: (1) With pure sulphuric acid, 13·50, 13·50, and 13·59 per cent. of nitrogen; (2) with a sample of commercial sulphuric acid, 14·12, 14·25, and 14·14; and (3) with another sample of commercial sulphuric acid, 15·8 and 15·2. Taking 13·5 per cent. as nearest to the truth, the result is very much too low in comparison with Dumas' process, which has stood the test of time. Although the majority of authors have obtained satisfactory results by Kjeldahl's process, and it is undoubtedly to be recommended in the case of the more readily decomposed organic compounds, as shown by the authors in the case of acetanilide, they are of opinion that in the case of the less easily decomposed compounds, the results have a tendency to be much too low.

D. B.

Kjeldahl's Method for the Estimation of Nitric and Total Nitrogen. By O. FÖRSTER (*Landw. Versuchs-Stat.*, **38**, 165—194; compare Abstr., 1889, 547 and 746).—*Estimation of Nitric Nitrogen.*—A weighed amount of a solution of potassium nitrate of known strength was evaporated to dryness in the flask used for the decomposition; in some cases the salt was weighed. When phenolsulphonic acid is used alone, the results are low, especially when an excess of phenol is employed. Very good results were obtained with phenolsulphonic acid and zinc-dust, but it was found that the addition of platinic chloride is not only unnecessary, but may readily give rise to a loss of nitrogen. The employment of zinc-dust requires great care owing to the violence of the reaction, and it is necessary to cool the flask (Märcker and Kühn, *Landw. Versuchs-Stat.*, **35**, 445). It was found preferable to use sodium thiosulphate. The potassium nitrate is treated with sulphuric acid containing 6 per cent. of phenol and shaken until the nitre is dissolved. The amount of acid used is 30 c.c. for 1 gram of the salt. When the solution is complete, pure crystallised sodium thiosulphate (3—5 grams) is added, and after the reaction is over, mercury (0·5 gram) and sulphuric acid (20 c.c. for 1 gram of substance) are added. The addition of phosphoric anhydride and of potassium permanganate is unnecessary. The decomposition is effected in an egg-shaped flask of 150—200 c.c. capacity, with a neck about 18 cm. long. The author considers the open receiver

usually employed for absorbing the ammonia to be unsafe, and recommends a wide U-tube of 500—600 c.c. capacity with bulbs. The reagents employed were examined for nitric acid, but were found not to contain sufficient to affect the results. It is not advisable to purify the sulphuric acid as recommended by Meldola and Moritz (*J. Soc. Chem. Ind.*, 7, 63), as the excess of nitrous acid cannot be entirely got rid of, and may give rise to a loss of nitrogen.

Experiments in which sulphosalicylic acid and sodium thiosulphate were used show that sulphosalicylic acid is preferable to phenolsulphonic acid (Scovell, Abstr., 1889, 308), one advantage being that the results are not affected by the presence of chlorine, which is of importance in the analysis of Chili saltpetre. The low results obtained when phenolsulphonic acid is used in presence of chlorides is attributed to the formation, and volatilisation, of chloropicrin; but this difficulty may be overcome by adding 10 c.c. of a 0·6 per cent. solution of silver sulphate to the nitrate solution before evaporating to dryness.

Estimation of Total Nitrogen.—Known amounts of potassium nitrate were added to various organic substances, such as starch, paper, oxalic acid, &c., and the nitrogen determined, using phenolsulphonic acid and sodium thiosulphate. The results were all very satisfactory with the exception of those obtained when olive oil was used, which were too low.

A very good indicator for use in nitrogen estimations can be made by extracting commercial litmus (80 parts) with 20 per cent. alcohol (1000 parts), and adding malachite-green. Most indicators are influenced by carbonic anhydride and by ammonium salts. Phenolphthaleïn cannot be used. N. H. J. M.

Quantitative Estimation of Nitric Acid by Electrolysis. By G. Vortmann (*Ber.*, **23**, 2798—2801).—A solution of the nitrate is placed in a platinum dish, together with crystallised cupric sulphate and dilute sulphuric acid, a feeble current of electricity is passed through the liquid until all the copper is deposited, and the solution is concentrated and distilled with excess of sodium hydroxide, the ammonia which is evolved being collected and determined in the usual manner. In the case of potassium nitrate, at least half its weight of crystallised copper sulphate should be employed; if less be taken, the current must be proportionately reduced. A salt of platinum or of mercury may be substituted for the cupric salt, or the positive electrode may be covered with copper. If relatively large quantities of nitrate are present, the direction of the current should be changed when all the copper has been deposited on the negative electrode; in these circumstances, a known quantity of sulphuric acid is added, and the excess remaining after the completion of the operation is titrated with one-fifth normal ammonia. The experiments were made in all cases with potassium nitrate, and the results obtained agree closely with the theory. J. B. T.

Estimation of Carbon in Organic Substances by a Wet Method. By J. Messinger (*Ber.*, **23**, 2756—2760; compare Abstr.,

1889, 80).—The substance is weighed in a small tube and placed in a flask of some 200 c.c. capacity containing 6—8 grams of chromic acid, so as not to touch the latter. The flask is fitted with a tap funnel, and is connected with a condenser inclined upwards. This is connected with a small combustion tube some 15 cm. long, drawn out at both ends, and containing copper oxide and lead chromate. This is joined to a drying apparatus containing both sulphuric acid and phosphoric anhydride, which is connected consecutively with a weighed potash-bulb apparatus, the ground tube of which is filled with soda-lime, with a weighed U-tube which contains the same substances, and lastly with an unweighed calcium chloride tube. A slow stream of air freed from carbonic anhydride is drawn through the apparatus, 50 c.c. of concentrated sulphuric acid is run on to the chromic anhydride, and the flask gently warmed until the anhydride dissolves. The decomposition of the substance then commences, and the flame is removed, but is replaced after 20 minutes, and the operation then continued for two hours. The gain in weight of the potash bulbs and soda-lime tube corresponds with the weight of carbonic anhydride derived from the combustion of the carbon in the substance examined. Good results were obtained with substances of varied chemical character. The small combustion tube must not be omitted, or the carbon will, in some cases, come out too low. C. F. B.

Method for Determining Alkalis in Presence of Sulphites. By J. Grant and J. B. Cohen (*J. Soc. Chem. Ind.*, **9**, 19—20).—A measured volume of hydrogen peroxide is run into a beaker, together with three or four drops of methyl-orange. As hydrogen peroxide is always slightly acid, a small quantity of a very dilute solution of sodium hydroxide (1 : 100) is added by means of a 1 c.c. pipette until the neutral point is reached. The requisite quantity of alkaline sulphite solution is next added, and boiled up at once, but gently. During the latter part of the boiling, the methyl-orange is bleached. The solution is cooled, a few more drops of methyl orange added, and the solution titrated with normal hydrochloric acid. From a series of experiments, the authors conclude (1) that the quantity of ordinary 10 per cent. hydrogen peroxide required depends on the percentage of sulphide present in the alkaline solution. The "caustic salts" of commerce contain about 50 per cent. of sulphite, hence it is sufficient to take 10 c.c. of commercial hydrogen peroxide for every 0·1 gram of the "salts" solution, although this gives twice the theoretical quantity of oxygen required to oxidise the sulphite to sulphate. For salts containing above 50 per cent. of sulphite, it is better to take double the volume of hydrogen peroxide. (2.) It is unnecessary to leave the mixture of alkaline sulphite solution and hydrogen peroxide for half an hour before boiling up, seeing that the increase in quantity of acid required for neutralisation is almost inappreciable. D. B.

Gas-Volumetric Analyses of Potassium Permanganate, Bleaching Powder, and Manganese Dioxide. By G. Lunge (*J. Soc. Chem. Ind.*, **9**, 21—24).—The author, in this paper, only treats

of those of the numerous uses of the nitrometer in which hydrogen peroxide is employed as the principal reagent, and although the methods he refers to have been previously mentioned, the paper in question gives such data as amount to a conclusive proof of the correctness of the results to be obtained by this analytical method.

1. *Standardising Potassium Permanganate with Hydrogen Peroxide in the Nitrometer.*—In this case it is necessary to work with acid solutions containing a large excess of sulphuric acid. The permanganate employed was made from pure crystals, and was as nearly as possible semi-normal, namely, 1 c.c. = 0·004 gram of oxygen. It was standardised with iron wire; with crystallised oxalic acid, purified according to Winkler's process, and dried to constant weight in a Victor Meyer's air-bath at 56°; and with ordinary commercial hydrogen peroxide. The results were as follows:—

With iron wire	1 c.c. = 0·003999	gram oxygen.
With oxalic acid	1 c.c. = 0·003997	,, ,,
With hydrogen peroxide.	1 c.c. = 0·004002	,, ,,

For 10 c.c. of permanganate, 30 c.c. of dilute sulphuric acid (1 : 5) and 10 c.c. of hydrogen peroxide should be used. The above numbers show that the standardising with hydrogen peroxide in the nitrometer is one of the most accurate methods, having the great advantage that it is carried out within an extremely short time without requiring a standard substance of accurately known composition.

2. *Estimation of Bleaching Powder or Bleach Liquor by means of Hydrogen Peroxide in the Nitrometer.*—The reaction which takes place is as follows:—$CaOCl_2 + H_2O_2 = CaCl_2 + H_2O + O_2$. It is not necessary to know the exact composition of the reagent, but, as it is desirable not to employ too large an excess, it is best to make a rough preliminary test by titrating the hydrogen peroxide with an excess of bleach solution. For analysis, the reagent should be diluted before use, so as not to give out more than 7 c.c. of oxygen per c.c., and it must be made distinctly alkaline with sodium hydroxide up to the point at which a flocculent precipitate appears. The reading should be effected quickly, say, five minutes after mixing the liquids, otherwise the results will be too high owing to the gradual evolution of more oxygen from the alkaline liquid. In order to find the percentage of available chlorine by weight, it is necessary to remember that every c.c. of gas evolved, reduced to 0° and 760 mm., represents 0·003167 gram of chlorine. In practice it is best to dissolve 7·917 grams of bleach in 250 c.c. of water, and use 10 c.c. of the solution for each test, when every c.c. of oxygen evolved will directly indicate 1 per cent. of available chlorine. This involves the use of a 50 c.c. nitrometer. It is shown that the estimations are just as accurate when water is employed in the nitrometer as when using mercury. From the results of a large series of comparative tests, the author infers that the nitrometric method yields quite as concordant results in the testing of bleach as Penot's method, although by the former process there is about 0·2 per cent. more chlorine found, and

this amount might be deducted as a constant from the nitrometric results to bring them into entire concordance with those obtained by Penot's method.

3. *Analysis of Manganese Ore or Weldon Mud by means of the Nitrometer.*—In this case the reaction must take place in an acid solution. The finely-powdered ore is put into the outside space of the flask, and first treated with dilute sulphuric acid in order to decompose any carbonates present. The hydrogen peroxide is then introduced into the inner tube, the flask attached to the nitrometer, and the contents shaken up until the colour of the residue indicates the end of the decomposition. With Weldon mud the change is instantaneous. The reaction is illustrated by the equation $MnO_2 + H_2O_2 + SO_4H_2 = MnSO_4 + 2H_2O + O_2$. Every c.c. of gas evolved corresponds with 0·003897 gram MnO_2. Results are quoted showing that this method gives as accurate results as the ordinary iron sulphate process; and although for commercial purposes the latter will doubtlessly retain its supremacy. the nitrometric process offers the great advantage of a saving of time as well as dispensing with all standard solutions.

D. B.

Volumetric Estimation of Manganese. By G. VORTMANN (*Ber.*, **23**, 2801—2803).—The manganous salt, together with 2—3 parts of potassium alum, is dissolved in water and treated with excess of one-tenth normal iodine solution and pure sodium hydroxide; after warming for 5—10 minutes on the water-bath, the solution is cooled, diluted to a known volume, an aliquot part filtered, acidified, and the excess of iodine titrated with sodium thiosulphate solution.

Ferric sulphate may be employed in place of the aluminium salt; with the manganese alone, the results obtained are considerably too low. Potassium manganous sulphate was used for the determinations, and the results obtained agree closely with the theory.

J. B. T.

Estimation of Cobalt and Nickel. By J. HOPE (*J. Soc. Chem. Ind.*, **9**, 375—377).—The process consists of two operations:—(1) separation and determination of the cobalt by the "phosphate" method; (2) determination of the nickel by electrolysis. The phosphate method was originally devised by Dirvell (Abstr., 1880, 287), but it was not until modified by Clark (Abstr., 1884, 498) that its value as a means of separation was appreciated. The cobalt having been separated and weighed as pyrophosphate, the nickel is determined in the clear blue filtrate contained in a tall form of beaker, and measuring about 200 c.c., in the following manner:—10 c.c. of strong aqueous ammonia is added, and the solution, after heating to about 70°, is immediately ready for electrolysis. For this purpose a battery of two $1\frac{1}{2}$-pint size Bunsen cells is found to give the requisite strength of current, and is capable of depositing about 0·15 to 0·20 gram of nickel per hour. The electrodes consist of a sheet of platinum, shaped in the form of a cone. to the side of which a piece of thick platinum wire is rivetted. and a spiral formed of the same kind of wire, terminating in a straight piece. The spiral is then inserted

in the solution, the cone is also suspended to cover, without touching, the spiral, taking care to have it wholly immersed in the solution. The battery is now connected, the cone with the zinc pole, and the spiral with the carbon pole, and the beaker covered with two halves of a watch-glass. The complete deposition of the nickel may be ascertained by drawing off a small quantity of the solution, which should not give the slightest coloration on addition of a drop of colourless ammonium sulphide. As soon as this is the case, the cone is removed, thoroughly washed in distilled water, then in alcohol, dried in a water-bath, and weighed. The weight of the coue having been previously noted, the increase found represents the weight of metallic nickel. D. B.

Analysis of Ferro-Aluminium and Aluminium Steel. By A. ZIEGLER (*Dingl. polyt. J.*, **275**, 526—528).—The analysis of ferro-aluminium may be effected by means of the process given by the author for ferro-chromium. Ferro-aluminium is composed of iron, aluminium, manganese, silicon, and carbon, and resembles ferro-tungsten in appearance. For analysis, 0·5 to 1 gram of the finely powdered and sifted sample is fused in a platinum crucible, half filled with freshly ignited hydrogen sodium sulphate. The melt is then extracted with hot water, aud the residue containing silica filtered and washed with a 1 per cent. solution of hydrochloric acid. It is then tested with sulphuric and hydrofluoric acids as to the presence of any original substance not fully attacked. Any tangible residue left after this treatment is re-fused with the above flux, and the aqueous extract added to the above solution. The mixture is now deoxidised with sodium hypophosphite (10 c.c. of a solution containing 1 part of NaH_2PO_2 in 2 of water), the alumina precipitated by the addition of pure zinc oxide (suspended in water), and separated from the ferrous salt by filtration. The precipitate is dissolved in hydrochloric acid, and reprecipitated. It is then redissolved in hydrochloric acid, and the alumina precipitated with ammonia, re-dissolved in hydrochloric acid and reprecipitated. To ensure the absence of zinc and iron, it is recommended to fuse the precipitate (after ignition) with sodium carbonate, extract with water, reprecipitate the aluminium with carbonic anhydride, and filter. The filtrate is acidified with hydrochloric acid, and any alumina contained therein precipitated with ammonia. The precipitates are dissolved on their respective filters with hydrochloric acid. The alumina in the joint solutions is then precipitated with ammonia and ammonium chloride.

The analysis of aluminium steel may be effected in a similar manner, 5 to 10 grams of substance being used. As fusion with hydrogen sodium sulphate does not, however, invariably decompose the steel completely, especially when the substance to be analysed is in the form of borings, the author prefers to dissolve the steel in hydrochloric acid, separate the silica in the usual way, and submit the clear solution to the above treatment. Hydrochloric acid may also be employed for dissolving ferro-aluminium. D. B.

Rapid Estimation of the Principal Constituents of Cow's Milk. By BALLARIO and REVELLI (*Bied. Centr.*, 1890, 540—541).—A comparison instituted between the results obtained by Soxhlet's aræometer and those obtained by the use of Marchand's lactobutyrometer, with the assistance of the tables corrected by the subtraction of 3·5 from every number, and the tables of Schmidt and Tollens, induces the authors to recommend the lactobutyrometer for all general purposes, so long as the percentage of fat lies between 1·3 and 4·5 per cent. The estimates of dry matter, as obtained by direct evaporation and by the use of Fleischmann and Morgen's formula as applied to the specific gravity, do not vary much the one from the other. For example, with a percentage of fat of 4·2, the range of differences found amounted to −0·07 to +0·33, when 46 samples were examined. Fleischmann's new formula (Abstr., 1885, 533) does not give such accurate results, the range of differences being +0·22 to −0·26. E. W. P.

Estimation of Ash in Sugars. By E. BOYER (*Compt. rend.*, **111**, 190—192).—5 grams of the sugar is mixed with 1 c.c. of water and heated gently, in order to convert it into caramel without carbonising it. It is then mixed with 2 c.c. of a solution of 25 grams of benzoic acid in 100 c.c. of alcohol of 90°, and is carefully heated until the alcohol is expelled. By gradually raising the temperature the sugar is carbonised, and the evolution of vapours of benzoic acid keeps the carbon in a very porous condition, so that it is readily burnt off in a muffle at a dull-red heat. This method removes the necessity for the uncertain corrections involved in the usual process. C. H. B.

Detection of Impurities in Alcohol. By E. MOHLER (*Compt. rend.*, **111**, 187—190).—The reagents which gave the best results are sulphuric acid, magenta acid sulphite, aniline acetate, and potassium permanganate.

Sulphuric acid should be added in a volume equal to that of the alcohol; with a larger proportion pure alcohol gives a coloration, with a lower proportion the reaction is less sensitive. The following are the minimum proportions per litre which can be detected:—furfuraldehyde, 0·010 gram; capryl alcohol, 0·050 gram; isobutyl aldehyde, paraldehyde, acetaldehyde, and isobutyl alcohol, 0·125; propionaldehyde, œnanthylaldehyde, valeraldehyde, and amyl acetate, 0·250; formylcarbinol, acetylcarbinol, heptyl alcohol, and amyl alcohol, 0·500 gram. Alcohol containing 0·1 per cent. of butaldehyde, acetone, propyl, isopropyl, butyl, and methyl alcohols, and ethyl acetate, propionate, butyrate, isobutyrate, valerate, caproate, œnanthylate, sebate, benzoate, and salicylate give no coloration.

Magenta bisulphite varies in its action, according to the proportion of acid which it contains; the following solution gives good results:—Magenta solution (1 : 1000) 30 c.c., sodium hydrogen sulphite 34° B. 20 c.c., sulphuric acid 3 c.c., water 200 c.c. 10 c.c. of the alcohol under examination is mixed with 4 c.c. of this solution and allowed to remain for half an hour; it will detect in alcohol of 50° the following minimum quantities of impurities per litre: acetaldehyde and

œnanthylaldehyde, 0·01 gram; valeraldehyde, 0·02; propionaldehyde and isobutaldehyde, 0·05; paraldehyde, furfuraldehyde, butaldehyde, and acetone, 0·50. Alcohols and ethers have no effect on the reagent; the colour developed is not proportional to the quantity of aldehyde present.

Aniline acetate is the special reagent for furfuraldehyde, and is not affected by other aldehydes, or by alcohols or ethers. Within somewhat wide limits the colour is independent of the proportions of aniline and acetic acid, but the best results are obtained by adding 10 drops of aniline and 2 c.c. of glacial acetic acid to 10 c.c. of the alcohol, allowing the mixture to remain for half an hour. The reaction will detect 1 part of furfuraldehyde in 1,000,000, and even in 10,000,000, and it may be applied in quantitative estimations.

Potassium permanganate in acid solution is immediately decolorised by paraldehyde, isobutaldehyde, and isobutyl alcohol. The reduction is very distinct, and is proportional to the quantity of these compounds present; it may, therefore, be applied in a quantitative manner. Acetaldehyde in the proportion of 1 in 1000 has no immediate reducing action on the permanganate. C. H. B.

Qualitative Test for Glycerol. By C. A. Kohn (*J. Soc. Chem. Ind.*, **9**, 148).—Advantage is taken of two characteristic reactions:—(1) the formation of acraldehyde by the distillation of glycerol with hydrogen potassium sulphate; (2) the red coloration produced with a solution of rosaniline, decolorised by sulphurous anhydride, by acraldehyde, as by all aldehydes. The delicacy of the reaction has been tested, with the result that it is possible to detect 0·015 gram of glycerol. The reaction is not given by any of the following substances:—Manitol, cane-, grape-, or milk-sugar, starch, dextrin, albumin, gelatin, stearic acid, and oleic acid, but the carbohydrates interfere with the delicacy of the test, owing to the fact that their distillation products with hydrogen potassium sulphate hinder the formation of the red colour with rosaniline solution. D. B.

Volumetric Estimation of Phenols. By J. Messinger and G. Vortmann (*Ber.*, **23**, 2753—2756).—A known quantity of the phenol is dissolved in such a quantity of soda solution that at least 4 mols. of soda are present for every 1 mol. of the phenol; the soda should be free from nitrite. The solution is then warmed to about 60°, and decinormal iodine solution added until a strong yellow coloration is produced. The solution is then shaken, and warmed if required, when a precipitate forms. The solution is then cooled, acidified with dilute sulphuric acid, and diluted to 250 or 500 c.c. An aliquot part, say 100 c.c., is filtered off, and the excess of iodine in it determined by titration with decinormal thiosulphate solution. The weight of iodine used in forming the precipitate, multiplied by a certain factor, gives the weight of phenol in the sample examined. The value of the factor is: for phenol, 0·123518; thymol, 0·2956772; β-naphthol, 0·37813106; and for salicylic acid, 0·1813266. In the case of these four phenols fairly accurate results were obtained.

C. F. B.

A Quantitative Reaction of Lignin. By R. BENEDIKT and M. BAMBERGER (*Monatsh.*, **11**, 260—267).—When wood is submitted to the action of hydriodic acid, as in Zeisel's process for determining methoxyl (Abstr., 1886, 493), it yields methyl iodide. Since pure cellulose gives no methyl iodide, and various woods give just the same amount after thorough extraction with water, alcohol, and ether as before, the authors regard those portions of the wood known collectively as lignin, as furnishing the methyl iodide. Coniferin, coniferyl alcohol, and vanillin occur in quantities too small to yield any considerable amount of methyl iodide.

The methyl-number of wood thus becomes an approximate indication of its lignin contents. Taking Schulze's number, 54·1 per cent., as the amount of lignin in oak-wood, and calculating from the methyl-number, 28·6, given by oak-wood, the methyl-number of pure lignin becomes 52·9. On this basis the authors have calculated the amount of lignin in the woods tabulated below, the results being compared with those of Schulze:—

		Lignin contents.	
Sample.	Mean methyl-number.	Benedikt and Bamberger.	Schulze.
Nutshells	37·4	70·0	65·9
Oak	28·6	54·1	54·1
Alder	28·9	54·6	52·0
White beech	26·4	49·9	51·6
Acacia	24·2	45·9	47·0
Pine	21·3	40·3	42·0

The methyl-numbers of a variety of woods have been determined by treating 0·3—0·6 gram of the finely-divided wood, both air-dried and dried at 100° in Benedikt and Grüssner's apparatus (this vol., 299). The numbers vary between 20 and 31, and are approximately the same in different samples of the same wood. A table of the numbers is given in the original paper.

It is interesting to note that the methyl-number of lignite is 22·1; that of brown coal, 2·6; and that of true coal, 0.

The method may be useful in analysing paper. A. G. B.

Isocholesterin. By E. SCHULZE (*Zeit. physiol. Chem.*, **14**, 522—523).—The cholestol reaction referred to in another paper is given, not only by cholesterin, phytosterin, and caulosterin, but also by the isocholesterin of sheep's wool, and the benzoyl compound of isocholesterin. W. D. H.

A New Method of Saponification. By A. KOSSEL and K. OBERMÜLLER (*Zeit. physiol. Chem.*, **14**, 599—601).—Sodium ethoxide is recommended as the most convenient reagent for the saponification of ethereal salts of the fatty acid series. In place of using sodium ethoxide as such, sodium wire may be added to the ethereal alcoholic solution of the fat with equally favourable results. W. D. H.

Determination of the Fatty Acids in Soap. By M. SAUPE (*Chem. Centr.*, 1890, ii, 126; from *Pharm. Centralhalle*, **31**, 314—315). —For the determination of the fatty acids in soap, the author recommends the following method, which is substantially the same as that employed by Liebermann and Wolff for the determination of fat in milk. 2 grams of the finely cut up soap is dissolved in a separating cylinder with 50 c.c. of water, 5 c.c. of hydrochloric acid is then added, and the free fatty acid is extracted with 54 c.c. of ether saturated with water. After the ether has separated, 20 c.c. is measured off into a beaker, the ether evaporated, and the residual fatty acids weighed.

J. W. L.

Detection of Salicylic Acid in Wine. By MEDICUS (*Chem. Centr.*, 1890, ii, 28—29; from *Pharm. Centralhalle*, **31**, 321).—The author has observed the ferric chloride reaction in wines which have been undoubtedly free from salicylic acid. He has found that this is due to the presence of a yellowish oil, volatile with steam, sparingly soluble in water, readily so in ether, which was obtained from a large quantity of grape juice. He recommends that only 50 c.c. of wine shall be extracted for salicylic acid, instead of 100 c.c. (as recommended by Röse), and that the residue of the extract shall be treated with at least 10 c.c. of water, instead of 5 c.c.

J. W. L.

Analysis of Diuretin. By G. VULPIUS (*Chem. Centr.*, 1890, ii, 27—28, from *Pharm. Centralhalle*, **31**, 311—314).—Under the name diuretin, a diuretic has lately been introduced, consisting of a double salt of sodium theobromine and sodium salicylate. It is prepared by dissolving 180 parts (1 mol.) of theobromine in a solution of 40 parts (1 mol.) of sodium hydroxide, and adding 160 parts (1 mol.) of sodium salicylate, after which the double salt is obtained by concentrating the solution, 362 parts being obtained.

Diuretin, $C_7H_7N_4O_2Na,OH\cdot C_6H_4\cdot COONa$, is colourless, odourless, and readily soluble in water; its physiological action is unaccompanied by other adverse influences, and is quite distinct from *caffeino-sodium salicylicum*. It should contain 4·97 per cent. of theobromine. The analysis consists in the estimation of the theobromine and salicylic acid.

The theobromine is determined thus: 2 grams of diuretin is dissolved in 10 c.c. of water in a porcelain dish, the solution neutralised with 5 c.c. of normal hydrochloric acid, and then rendered just alkaline with one drop of dilute ammonia. It is frequently stirred for three hours at the ordinary temperature, and the theobromine may then be transferred to a tared filter, the filtrate being used to wash into the filter what remains in the dish; gentle suction will remove the last portions of the filtrate, and the theobromine is finally washed with 2 portions of 10 c.c. of cold water, dried at 100°, and weighed. The author has found that the weight varies between 0·82 and 0·83 gram of theobromine in the case of pure diuretin, 0·13 gram remaining in the filtrate and washings, which together represent 48 per cent., and he considers that at least 4[illegible]·5 per cent.

should be found. The theobromine should melt when carefully heated, should sublime, should leave no residue when burnt, and should dissolve readily in sodium hydroxide.

To determine the salicylic acid, the filtrate from the theobromine, together with the washings, is shaken in the separating funnel with 30 c.c. of ether, 2 grams of 25 per cent. hydrochloric acid is added, again shaken, separated, and the ether distilled off; the salicylic acid remaining should weigh 0·77 gram.

To prove the absence of a caffeïne preparation, 1 gram of the suspected diuretin is dissolved in 5 c.c. of water, and neutralised with hydrochloric acid, when theobromine should cause a milky precipitation, which should redissolve readily in aqueous soda, and if the mixture be shaken with its volume of chloroform, not more than 0·005 gram of residue should remain on evaporation of the latter.

J. W. L.

Quantitative Estimation of Colouring Matters by means of their Absorption Spectra. By T. L. Patterson (*J. Soc. Chem. Ind.*, **9**, 36—41).—In 1873 the author devised a method for estimating the amount of colouring matter in solutions which gave band spectra, by adapting a glass tube to the low power objective of a microscope, which worked vertically in a larger tube fitted to the sub-stage. On examining the light transmitted through a coloured solution placed in the lower tube by means of a spectrum eye-piece, having a comparison prism, over which was adjusted a sealed tube containing the standard solution, he was able to determine the height of a column of liquid of known strength which gave the same band absorption as the tube over the comparison prism. The height of the column of liquid was adjusted by means of the sub-stage pinion, the head of which was graduated for the purpose. On placing another solution of unknown percentage, but known strength, in the sub-stage tube, and adjusting the height of the column to give the same absorption as before, the two spectra being viewed alongside each other in the eye-piece, it was easy to calculate the value of the unknown one. The author used this apparatus occasionally, but the method is tedious and requires very careful adjustment of the light and all the parts of the instrument, in addition to which the separate comparison of two columns of liquid against a standard necessitates two readings, and consequently doubles the errors. In order to avoid these, he tried to adapt a slit and spectrum eye-piece to Laurent's colorimeter, and after some difficulty succeeded in fitting an adjustable slit just over the reflecting prisms, and by adapting the prismatic eye-piece of a microspectroscope, obtained an instrument which worked perfectly. The slit opens out wide, and, as now designed, the instrument may be used with the eye-piece suited for each, either for colorimetrical or spectroscopic work, qualitative or quantitative. In using the instrument, light reflected from the mirror beneath passes axially up through the solutions in the two tubes and movable columns, where it is received on the plane faces of two prisms, cut so as to totally reflect the light twice at right angles. Both beams now pass the slit in a divided "slice" of light, which is analysed by a direct-vision

spectrum eye-piece, in which two spectra of equal intensity are seen. Gas or lamp light is better for this work than daylight, as it has no absorption lines to interfere with the bands; and the less refrangible end of the spectrum is brighter than with any but direct solar light. It is best to use a screen to shade extraneous light from the eyes. A little micrometer is adapted to the eye-piece by which the bands or lines can be measured or mapped. The Fraunhofer and bright line spectra can of course be examined as well with this instrument as with any other, but the dispersion being necessarily small, it is not possible to measure the lines with any degree of accuracy. This spectroscope is properly adjusted for work and ready for use, when the slit has a proper width, and the two spectra are seen in the eye-piece to have an equal intensity, and when the index of each cylindrical column points to zero on the scales, with the base of the column just touching the bottoms of the glass tubes. If now a solution of any colouring matter which absorbs light selectively, say, a dilute alkaline alcoholic solution of alizarine of known strength, be run gently into one tube from a pipette, the two characteristic bands which this body displays will be seen to come gradually into view on turning up the milled head of the glass cylinder and allowing the liquid to flow in between the base and the bottom of the glass tube. By raising or lowering the cylinder it is easy to get the exact thickness of liquid at which the bands are seen to the best advantage. If another solution of alizarine of unknown strength—it may be more or less concentrated—be run into the other tube, and the milled head turned so as to raise the glass column, a point is easily reached at which the two spectra viewed in the eye-piece are seen to be equal. On reading off the heights of the two columns, the strength of the unknown one is found to be inversely proportional to the height of the column and the strength of the known solution. Assuming the height of the standard column to be a, and its strength b, the height of the unknown column c, and its strength x, then x is found by the formula $\frac{ab}{c} = x$.

D. B.

Gantler's Method of Estimating Tannin. By H. R. Procter (*J. Soc. Chem. Ind.*, 9, 260—261).—Referring to Gantler's process of estimating tannin, in which the determination is made with permanganate in a boiling solution (compare this vol., p. [illegible]), the author finds that the amount of permanganate consumed is materially influenced by the excess of permanganate added and the amount of boiling to which it is submitted. The author considers it probable that by adherence to a rigid scheme of operation concordant results might be obtained, but such results could have at best but a comparative value, and no greater claims to accuracy than those obtained by the Löwenthal method.

D. B.

Analysis of Straw. By A. Hébert (*Ann. Agron.*, 16, 358—371).—See this vol., p. 1459.

Examination of Acid and Compressed Fodders, and the Estimation of Total Nitrogen in them. By J. König (*Landw.

Versuchs-Stat., **38**, 227—234).—According to Kellner (*Landw. Versuchs-Stat.*, **32**, 56) there is a considerable loss of nitrogen in acid fodder if the ammoniacal nitrogen is not taken into account, and he suggests treatment with hydrochloric acid to prevent it. Woll (Abstr., 1889, 1030) found that the treatment with acid had no appreciable effect on the results. The following method is recommended:—The substance is cut up and mixed, and 100 or 200 grams or more, according to whether it is a material with fine or coarse stalks, weighed out, and gradually mixed with a mixture of 3 vols. of strong and 2 vols. of fuming sulphuric acid (100—150 c.c.) in a porcelain dish, which, with the pestle, was previously weighed. The solution of the substance may be aided by heating on a sand-bath. When a uniform paste is obtained, the whole is covered with a large watch-glass and left to cool in air free from ammonia. It is then weighed, and 30—60 grams (corresponding with 2—4 grams of dry matter) transferred to a flask of 500—600 c.c. capacity, for determination of nitrogen by Kjeldahl's method; 10—15 c.c. of sulphuric acid is added, and the whole heated over a small flame to drive off the water. The rest of the process is carried on in the usual manner. Very concordant results are obtained.

Farmyard manure may be analysed in a similar manner if it does not contain too coarse stalks. A small cube is first cut out with a sharp spade, well mixed in a dry barrel, a smaller sample taken from it, and 200—400 grams of this weighed and treated with acid.

Direct nitrogen determinations may also be made in liquids such as milk, urine, &c., by evaporating off the water in hard flasks after the acid has been added.

In estimating the free acids in acid and compressed fodder (sweet ensilage), 100 or 200 grams of the very finely-cut substance is kept for 5 to 6 hours in a 1 or 2 litre flask with 700 or 1500 c.c. of water. The flask is filled to the mark, the contents mixed, and filtered. 100 or 200 c.c. of the solution is titrated with $\frac{1}{4}$ or $\frac{1}{10}$ normal soda, with phenolphthaleïn as indicator; with strongly-coloured solutions litmus paper may be used. The volatile acid is determined by distilling 200 c.c. until 50 c.c. remain, and titrating. The method is not exact, but the results are relatively correct.

To estimate fat, the substance extracted by ether should be shaken with water at 50—60°, filtered, and washed with warm water; it is then washed with absolute alcohol and finally with ether. The alcoholic ethereal solution is then evaporated down, and the residue dried at 100°, and weighed. N. H. J. M.

Analysis of Bootblacking. By F. M. Horn (*Chem. Centr.*, 1890, i, 950; from *Zeit. Nahrung. und Hygiene*, **4**, 60).—The blacking is treated with boiling water, which dissolves out the portions soluble; the residue is then extracted with chloroform, which dissolves out the fat, and, finally, the residue is ignited, the mineral matter being thus determined, the difference being organic matters or carbon. In the aqueous extract any glucose may be determined according to Herzfeld's method, the glycerol by Benedikt and Cantor's method, and the free acid, if volatile, distilled and estimated by titration, any free

sulphuric acid remaining in the retort. A sample had the following composition:—Calcium phosphate, 21·06 per cent.; gypsum, 3·02; sand, 3·07; carbon, 2·41; fats and fatty acids, 6·08; invert-sugar, 3·47; glycerol, 0·75; acetic acid, 2·10; free sulphuric acid, 1·01; water, 56·40; from which the author calculates the blacking to be made up from 80 grams of molasses mixed with 14 grams of sulphuric acid and 10 grams of acetic acid, and then added to 280 grams of fine bone-black and 60 grams of whale oil, water being finally added to the desired consistence.

J. W. L.

ERRATA.

Vol. XLVIII (1885).

Page	Line		
1080	19	from bottom, *for*	"papaveric acid" *read* "papaverinic acid."

Vol. LVI (1889).

Page	Line		
758	7	from top, *for*	"degrees" *read* "degree."
950	14	„ „ „	"nitrate" „ "nitrite."
953	2	„ bottom, „	"isopropylcarbamide" *read* "isopropylcarbamine."
954	18	„ top, „	"$NH_2Pr^{\beta}\cdot NO_2$" *read* "$NH_2Pr_2^{\beta}\cdot NO_2$."
963	8	„ „ „	"$NH_2\cdot CO\cdot NPr_2^{\alpha}$" *read* "$NH_2\cdot CO\cdot NPr_2^{\beta}$."
981	16	„ „ „	"benzenemetadisulphontetrabromamide" *read* "benzenemetadisulphotetrabromamide."
985	9	„ bottom, *before*	"The 6 : 2 : 1-acid" *insert* "(3)".
1016	4	„ „ *for*	"papaveronic acid" *read* "papaverinic acid."
1071	3	„ „ „	"Terpine" *read* "Terpene"
1072	21	„ „ „	"dextro-" „ "lævo-."

ERRATA.

Vol. LVIII (1890).

Page	Line				
53	9	from	bottom,	*for*	"$C_{10}H_4{<}\begin{smallmatrix}COCl\\OPOCl_2\end{smallmatrix}$" *read* "$C_6H_4{<}\begin{smallmatrix}COCl\\OPOCl_2\end{smallmatrix}$."
113	17	,,	top,	,,	"Egermann" *read* "Eyermann."
,,	2	,,	bottom,	,,	"Egermann" *read* "Eyermann."
122	21	,,	top,	,,	"oxalenediazoximedibenzyl" *read* "oxalenediazoximedibenzenyl."
170	4	,,	bottom,	,,	"camphor" *read* "quinine."
357	5	,,	,,	,,	"propionylpropionaldehyde" *read* "propionylpropaldehyde."
402	11	,,	,,	,,	"Scopola" *read* "Scopolia."
,,	9	,,	,,	,,	"Scopola" *read* "Scopolia."
414	6	,,	,,	*before*	"now added" *insert* "is."
492	21	,,	top,	*for*	"Hoffmann's" *read* "Hofmann's."
721	8	,,	bottom	,,	"$NH_2{\cdot}NMe$" *read* "$NH_2{\cdot}NHMe$."
873	bottom,			,,	"*β-diterpolactone acid*" *read* "*β-diterpolactonic acid.*"
884	17	from	bottom,	,,	"chloroxythymoquinone" *read* "chlorohydroxythymoquinone."
893	17	,,	top,	,,	"*Dinitrodiphenylsalicylic acid*" *read* "*Dinitrophenylsalicylic acid.*"
898	20	,,	top,	*delete*	"O. Doebner and."
901	21	,,	bottom,	*for*	"Pyrrolene" *read* "Pyrroline."
907	7	,,	top,	,,	"C. W. Zanetti" *read* "C. U. Zanetti."
929	2	,,	,,	,,	"F. Walls" *read* "F. Watts."
947	9	,,	bottom	,,	"unstable" *read* "stable."
1090	12	,,	top,	*after*	"*disulphide*" *insert* "*hydrochloride.*"
1131	10	,,	,,	*for*	"dihydroterephthalic acid" *read* "dihydroterephthalate."
1136	22	,,	,,	,,	"β-phenylmaleïc" *read* "β-phenylmalic."
1150	5	,,	bottom,	*delete*	"J. Wislicenus and."
1156	3	,,	top,	*for*	"pyrroyl" *read* "pyrryl."
,,	6	,,	,,	,,	"pyrroylpyrotartaric" *read* "pyrroylpyruvic."
,,	17	,,	,,	,,	"pyrroylpyrotartaric" *read* "pyrroylpyruvic."
1178	2	,,	,,	,,	"1896" *read* "1890."
1190	10	,,	bottom,	,,	"**301**" ,, "301."
1195	7	,,	,,	,,	"spurting" *read* "spirting."
1203	2	,,	,,	,,	"Aslanoglon" *read* "Aslanoglou."
1477	14	,,	,,	,,	"Gantler" *read* "Gantter."
,,	15	,,	,,	,,	"Gantler" *read* "Gantter."

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